ELECTRO-ANALYTICAL STUDIES OF POLYANILINE : POLYAMIDE COMPOSITES

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

in

Applied Chemistry

By

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2007

To,

Abbi-Ammi

(Who offered their fingers when
I was trying to stand on my legs)

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Certificate

This is to certify that the work embodied in the dissertation entitled "Electro-analytical studies of polyaniline:polyamide composites" is the original contribution of Mr. Mohd. Khalid, carried out under my guidance and supervision and is being submitted in partial fulfillment of the requirement for the award of degree of Master of Philosophy in Applied Chemistry from Aligarh Muslim University, Aligarh. This work has neither been submitted, nor is it being submitted, for any other degree.

Dated: January 15, 2007

(Faiz Mohammad)
Supervisor

Acknowledgements

*First of all, I am highly indebted and grateful to my Lord "**Almighty Allah**" who blessed me with innumerable favour of academic work and produce in its present form.*

*It is a matter of great pride for me that I have got the kind supervision of **Dr. Faiz Mohammad** to complete my research work, his kind assistance, excellent guidance, valuable suggestions and whole-hearted support, helped me a lot through out research work. As my scientific supervisor he led me into dynamic world of Polymer Science, literally by fingers. I am and will remain indebted and shall follow his footprints in future.*

*It gives me great gratification to record thanks and heartiest regards to **Dr. Ali Mohammad** (Chairman) and the **teachers** of Department of Applied Chemistry for their valuable suggestions and encouragement during the entire period of this work.*

I have great passion to record my thanks and acknowledge the assistance and guidance extended to me by Farmanur Rahman Khan, S.M.A. Badruddin (Department of Zoology, AMU) and Arshad Ali

(Department of Plant Protection, AMU) for their magnanimous generosity, co-operation and brotherly help, whenever I needed.

I express thanks from bottom of my heart to my colleagues, Atika, Inamuddin, Tabassum, Azharullah, Zafar, Shagufta, Shahid Parvez, Mohd Omaish, Abdul Moheman, Inamur Rehman and specially Anis for his good and cordial company, healthy discussions and helping attitude during the study.

Friends are always fundamental unit of life. I am extremely lucky enough in this sense. I ventilate my ovation to my best friends, Mohd. Feeroz Ghazi, Dr. Mohd. Ahmad and Mohd. Rashid.

I owe a great debt to my father for their savvy tutelage and benedictions throughout my whole academic peregrination and sustenance. I feel pride and privilege for my beloved mother and sister Rafai for their kind love, support and cooperation during the persuasion of this research work.

(Mohd Khalid)

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1. INTRODUCTION

1.1. Polymers

The words polymer is derived from two Greek words, 'poly' which means many and 'mers' which means parts. So a polymer may be defined as long chain molecule produced by repeated joining of small units. In some cases, the repetition is linear while in others may be branched or cross-linked [1-3]. The smaller structural units are called monomers and they are covalently bonded together in any conceivable pattern. In certain cases, it is more accurate to call the structural or repeat unit, a monomer residue because some atoms may be eliminated from simple monomeric unit during polymerization process.

The essential requirement for a small molecule to qualify to be a monomer or "building block" is the possession of two or more bonding sites, through which each can be linked to other monomers to form the polymer chain. The number of bonding sites is referred to as the *functionality* of the monomers. Monomer, such as hydroxy carboxylic acid (HO—R—COOH) molecules through the hydroxyl and carboxylic groups, forms a linear polymer and the polymerization reaction in this case involves a series of simple organic reactions similar to:

$$R\text{-}OH + R'\text{-}COOH \rightleftharpoons R'\text{-}COO\text{-}R + H_2O \qquad (1)$$

The presence of double bond makes a vinyl compound bifunctional which on activation by some free radical or ion leads to the polymer formation:

$$CH_2{=}CHCl + R^{\cdot} \longrightarrow RCH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}CHCl^{\cdot}{\sim} \qquad (2)$$

Bifunctional monomers form linear polymers, however, the polyfunctional monomers i.e. having three or more bonding sites such as glycerol $CH_2(OH)$-$CH(OH)$-$CH_2(OH)$, produce branched, cross-linked polymers that contain three-dimensional network of both the branches and cross-links [4].

When only one type of monomer is used to produce a polymer, the product is called a *homopolymer,* normally referred to simply as a polymer. If the chains are composed of the two types of monomers, material is known as a *copolymer,* and if three different monomers are incorporated in one chain a *terpolymer* results.

Copolymers prepared from bifunctional monomers can be subdivided further into four main categories [5]:

(a) Statistical copolymers where the distribution of the two monomer residues in the chain is essentially random but influenced by the individual monomer reactivities.

~ ABAABABBBABAABABBBABAAAB ~

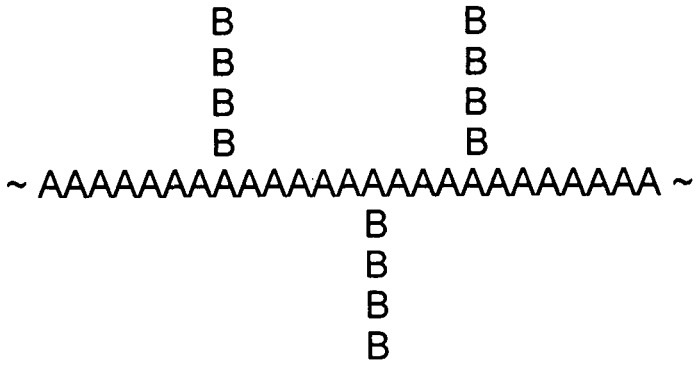
(b) Alternating copolymers with a regular placement along the chain.

~ ABABABABAABABABABAB BABABAB ~

(c) Block copolymers comprised of substantial sequences or blocks of each monomer

~ AAAAAAAAAABBBBBBBBAAAAAAAA ~

(d) Graft copolymers in which blocks of one monomer are grafted on to the backbone of the other as branches.

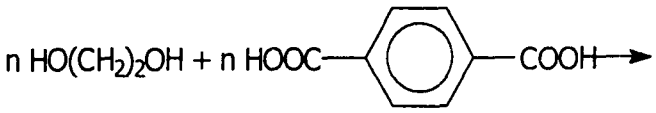


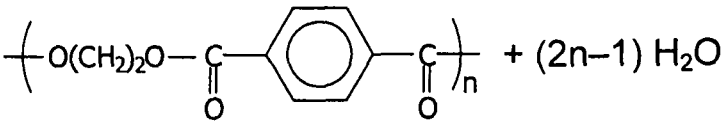
1.2. Synthesis of Polymers

A process used to convert monomers molecules into a polymer is called polymerization and the two most important type of polymerizations, viz. step-growth and chain polymerization, involve the condensation and addition reactions respectively.

1.2.1. Step-growth polymerization

A step-growth polymerization is used for monomers with functional groups such as –OH, –COOH, –COCl etc. and is normally, but not always, a succession of condensation reactions. Consequently, the majority of polymers formed in this way differ in chemical composition slightly from the original monomers because a small molecule is eliminated in the each step of the reaction, e.g. the reaction between ethylene glycol and terephthalic acid produces polyester better known as "Terylene".

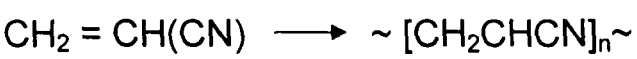




(3)

1.2.2. Addition polymerization

The addition polymerization, for olefinic monomers, involves chain reactions, which convert the monomers into polymers by stimulating the opening of the double bond with a free radical or ionic initiator. The product then has the same chemical composition as that of the starting material, e.g. acrylonitrile produces polyacrylonitrile without elimination of any small molecule during polymerization. The length of the molecular chain, which will depend on the reaction conditions, can be obtained from the measurements of molar masses of the polymer [5].



(4)

1.3. Electrical Conductivity in Materials

In many materials, such as crystals, stretched polymers or liquid crystals, macroscopic properties such as strength, optical and electrical properties generally depend on direction. They are said to be anisotropic. Similarly, the electrical conductivity of materials may depend on the direction of measurement and can be anisotropic. Three simple carbon compounds are diamond, graphite and polyacetylene. They may be regarded, respectively, as three, two and one-dimensional forms of carbon materials. Diamond and

graphite are modification of pure carbon, while one hydrogen atom is bound to each carbon atom in polyacetylene.

Diamond containing only σ-bonds, is an insulator and its high symmetry gives it isotropic properties. Graphite and polyacetylene both have mobile π-electrons and are highly anisotropic metallic conductors when doped. The conductivity is about one million times greater along the plane of the graphite rings than at right angle to the plane i.e. σ (parallel) / σ (perpendicular) = 10^6. Correspondingly, the conductivity of stretch-orientated polyacetylene is some 100 times higher in the stretch direction than perpendicular to it. The smaller anisotropy compared to graphite, i.e. non-vanishing σ(perpendicular), could suggest, "short-circuiting" across the chains. Since the polyacetylene chains are not infinite, contacts between them are important if the material has to be macroscopically conductive. This could thus explain the lower conduction anisotropy of polyacetylene compared to graphite.

Anisotropy is also interesting in other contexts of stretch aligned polymers. When the absorption of light is anisotropic the material acts as a polarizer. Also, the mechanical strength of such a polymer, is anisotropic, aligned polyacetylene fibers are known to be very strong along of the direction of orientation [6].

1.4. Electroactive Polymers

Inherently, organic polymers with all-carbon back bones are insulators and can be used as encapsulating materials when a medium of high resistivity is required, such as in the coating for

cables and electrical wiring. It has been found that the resistivity can be decreased if a composite of the polymer with carbon black or finely divided metal is formulated but the conduction in these cases takes place via the filler and not through the polymer, which merely acts as a supporting matrix. Incorporation of such fillers may reduce the mechanical strength of the polymer.

In 1977, the first major breakthrough was achieved when it was discovered that polyacetylene, which is a very poor conductor in the pure state, could be turned into a highly conductive polymer by conversion of it into its salt form on reacting with I_2. The result was a dramatic increase of over 10^{10} order of magnitude in conductivity. As conduction appears due to the movement of electrons through the polymer, this discovery has added an exciting new dimension to the rapidly expanding area of synthetic polymers. Other polymers that display similar characteristics are usually polyconjugated structures, which are insulators in the pure state but can be converted into polymer salts with electrical conductivities comparable to metals when treated with an oxidizing or a reducing agent.

Some idea of the conductivities (σ) of the materials is given in **Figure-1** where σ varies from 10^{-18} Scm^{-1} for a good polymeric insulator (polytetrafluoroethylene) to ~10^{6} Scm^{-1} for a metallic conductor (copper) [5].

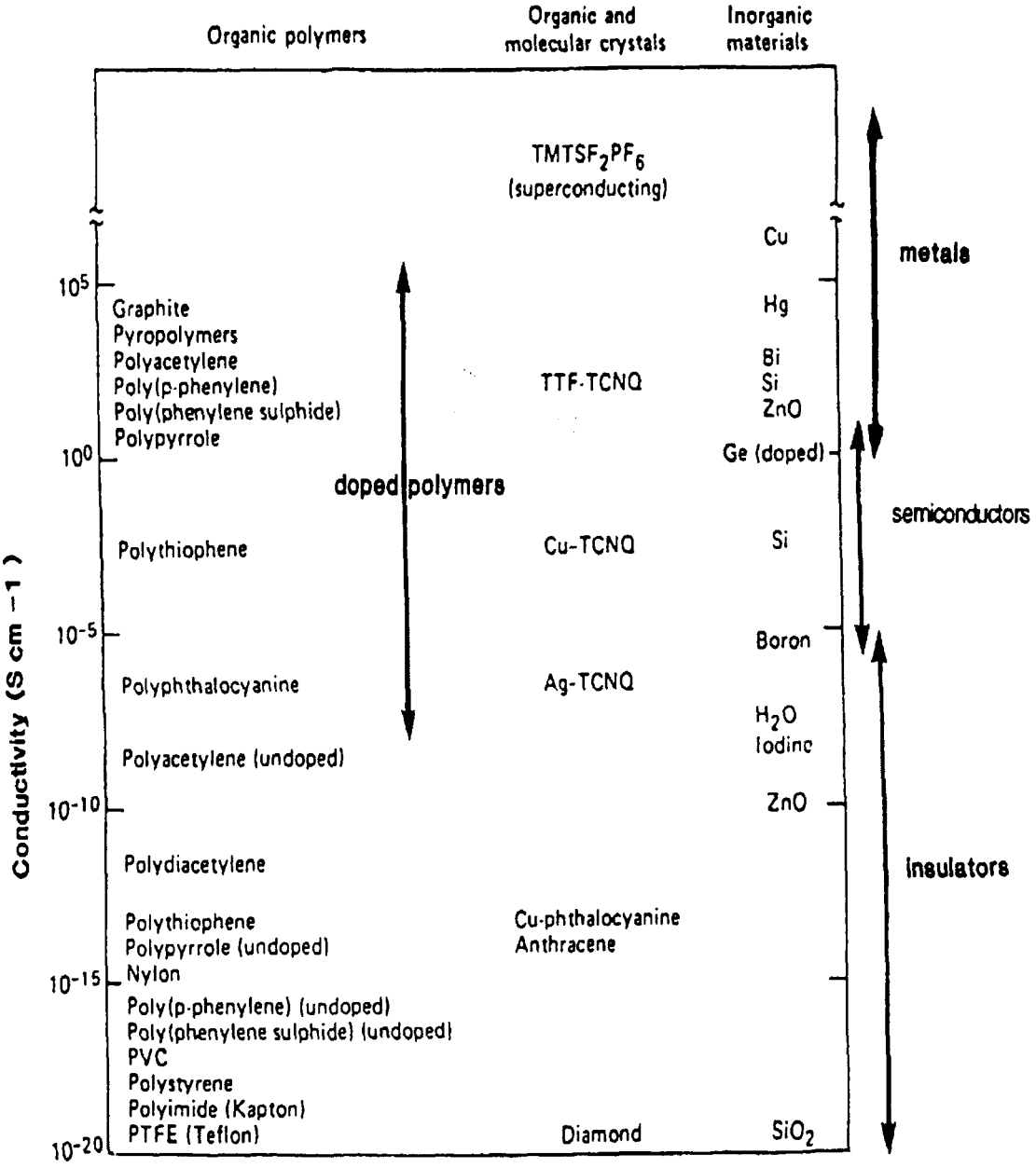


Figure-1. Electrical conductivities (Scm^{-1}) of polymers and some other important materials [5].

1.5. Conduction Mechanisms

Electrical conductivity is a function of the number of charge carriers of species "i" (n_i), the charge on each carrier (ε_i) and the mobility of the charge carriers (μ_i) as given under:

$$\sigma = n_i \varepsilon_i \mu_i \qquad (5)$$

Conduction in solids is usually explained in terms of the band theory which postulates that when atoms or molecules are aggregated in the solid state, the outer atomic orbitals containing the valence electrons split into bonding and antibonding orbitals and mix to form two series of closely-spaced energy levels. These are usually called the valence band and the conduction band respectively. If the valence band is only partly filled by the available electrons, or if the two bands overlap so that no energy gap exists between them, then application of potential will raise some of the electrons into empty levels where they will be free to move throughout the solid thereby producing a current. This is the description of a conductor.

On the other hand, the valence band is full and is separated from the empty conduction band by an energy gap, then there can be no net flow of electrons under the influence of an external field unless electrons are elevated into the empty band and this will require a considerable expenditure of energy. Such materials are either semiconductors or insulators, depending on how large the energy gap is and the majority of polymers are insulators due to the large band gap. The band model thus assumes that the electrons are delocalized and can extend over the lattice **Figure-2**.

When we come to consider electronic conduction in polymers, band theory is not totally suitable because the atoms are covalently bonded to one another, forming polymeric chains that experience weak intermolecular interactions. Thus, macroscopic conduction will require electron movement, not only along chains but also from one chain to another [5].

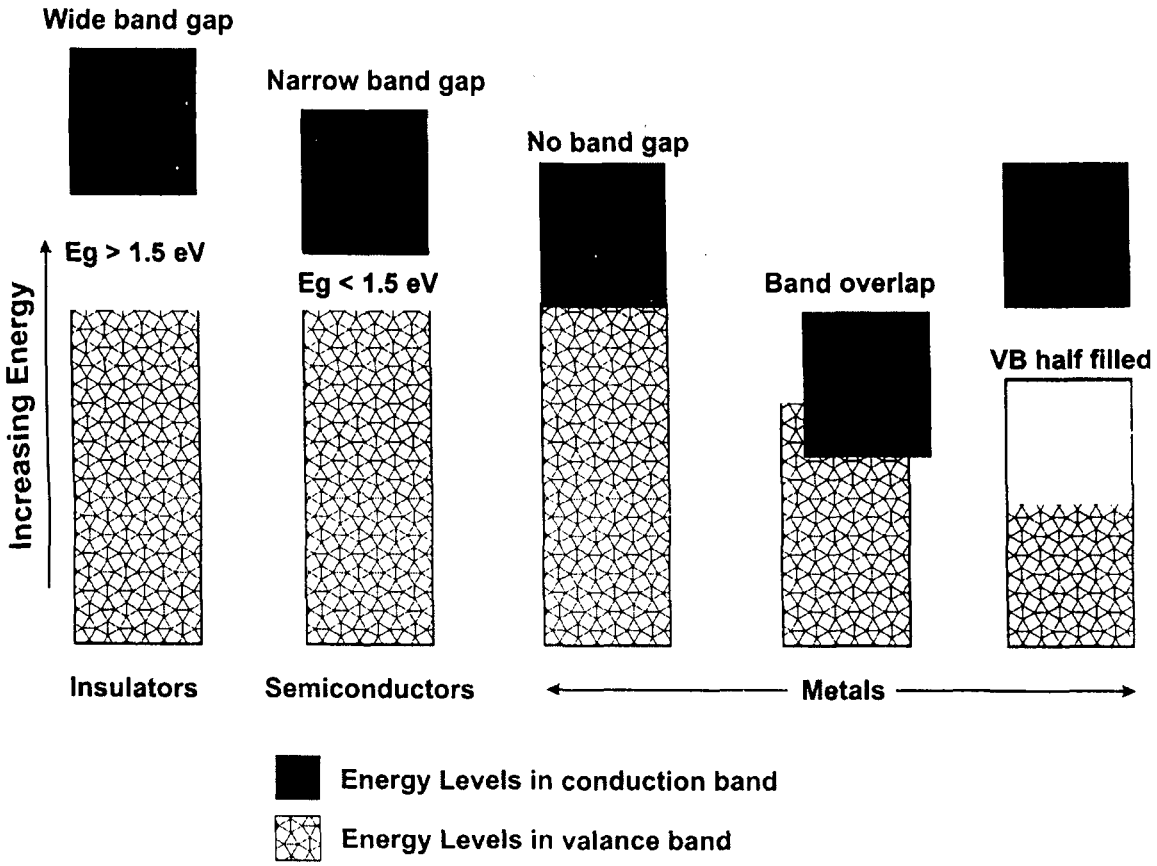


Figure-2. Simple band picture explaining the difference between an insulator, a semiconductor and a metal [5].

1.6. Doping in Conjugated Polymers

In order to conduct, a polymer must have a conjugated backbone for easy movement of charge carriers. However, the conjugated polymers do not contain any intrinsic charge-carriers, charge-carriers have to be provided extrinsically, typically by a charge transfer process, generally knows as 'doping'.

Polymers have the electronic profiles of either insulator or semiconductors; thus the band gap in a fully saturated chain such as polyethylene is 5 eV and decreases to about 1.5 eV in the fully conjugated system of polyacetylene. The respective intrinsic conductivities are 10^{-17} Scm^{-1} and ~ 10^{-8} Scm^{-1}, both of them are very low. Conjugated polymers can be made conductive either by oxidizing or reducing the polymer using a suitable reagent. The band theory model would explain the increased conductivity as either removal of electrons from the valence band by the oxidizing agent, leaving it with a positive charge, or donation of an electron to the empty conduction band by a reducing agent. These processes are called p-type doping and n-type doping respectively.

This explanation is an over-simplification, as the conductivity in polymers is associated with charge carriers that do not have free spins, rather than the expected unpaired electrons detected in metals, so a modified model must be developed. This will be explained when the individual conducting polymers will be described.

While the addition of a donor or acceptor molecule to a conjugated polymer is called "doping", the reaction, which takes place, is actually a redox reaction and is different from the doping of

Si or Ge in semiconductor technology where there is substitution of atoms in the lattice. The terminology in common use will be retained here also but it should be remembered that the doping of conducting polymers involve the formation of a polymer salt and that this can be effected either by exposing the polymer to the dopant in solution or in gaseous form or by electrochemical methods. The reaction can be represented in the generalized case for oxidation by:

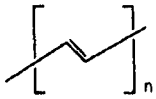
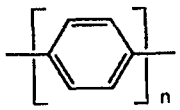
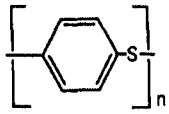
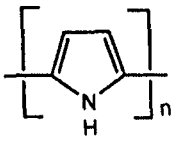
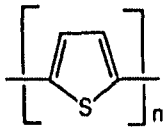
$$P \xrightarrow[X^+A^-]{\text{Oxidation}} P: X^+/A^- \qquad \text{p-type} \qquad (6)$$

where P represent a section of polymer chain. The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron, the distinction between them will be explained later. This step may then be followed by a second electron transfer with the formation of dication (or dianion) known as bipolaron. Alternatively, after the first redox reaction, charge transfer complexes may form between charged and neutral segments of the polymer when possible.

$$P \xrightarrow[X^+A^-]{\text{Reduction}} P: A^-/X^+ \qquad \text{n-type} \qquad (7)$$

The general principles can best be illustrated by examining specific examples, in particular polyacetylene, which has been studied intensively. The reactions between conjugated polymers and oxidants (p-type doping by an acceptor) or reductants (n-type doping by a donor) have been observed to cause a dramatic increase in electrical conductivity as evident from **Table-1**.

Table-1. Structures and conductivity of doped conjugated polymers [5].

Polymer	Structure	Typical method of doping	Typical conductivity (Scm^{-1})
Polyacetylene		Electrochemical, Chemical (AsF_5, I_2, Li, K)	500 – $1.5x10^5$
Polyphenylene		Chemical (AsF_5, Li, K)	500
Poly(phenylene sulphide)		Chemical (AsF_5)	1
Polypyrrole		Electrochemical	600
Polythiophene		Electrochemical	100

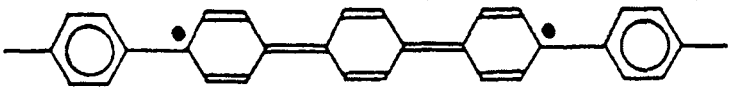
Doping is a multi-stage process, involving electron removal from polymer chain and typically maximum up to 50%. The charge-carriers in the form of radical cations (p-type) or radical anions (n-type) are thus produced on the polymer chains, which are called polarons (with spin) and bipolarons/solitons (spinless) at low and high dopant concentrations respectively as shown, for example, in case of polyphenylene **Figure-3**and the effect of dopant concentration on number of spins and electrical conductivity is shown in **Figure-4**.

The commonly used oxidants (p-type dopant) may include $HClO_4$, $FeCl_3$, AsF_5, I_2, NH_4BF_4, SO_3CF_3, HCl, HNO_3, H_2SO_4, H_3PO_4 etc. whereas reductants (n-type dopants) may include Li, K, Na etc. A general equation for doping of a conjugated polymer may given by the following chemical reaction [5,7].

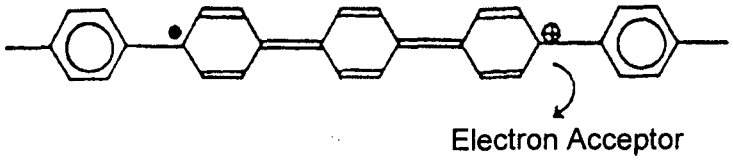
$$P + 2FeCl_3 \rightarrow P^+: FeCl_4^- + FeCl_2 \quad (8)$$

$$P + Na \rightarrow P^-: Na^+ \quad (9)$$

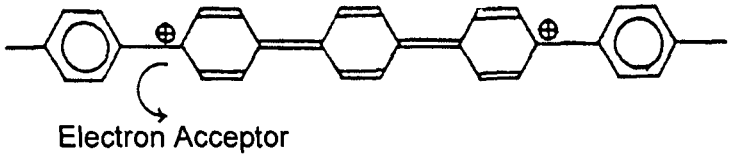
1. An unstable diradical with spin and without charge.



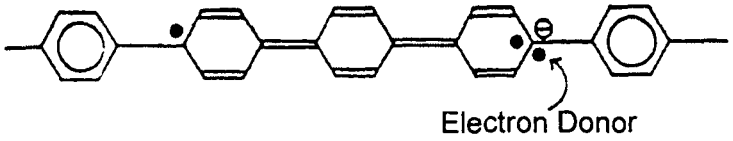
2. A stable polaron 'p-type' with spin charge.



3. A stable bipolaron 'p-type' with charge and without spin.



4. A stable polaron 'n-type' with spin and charge.



5. A stable bipolaron 'n-type' with charge and without spin.

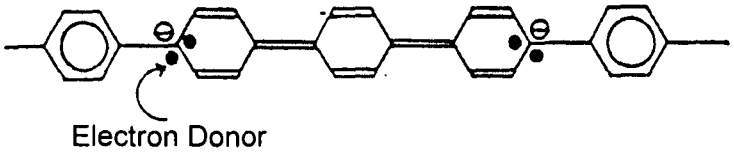


Figure-3. A schematic diagram of evolution of charge-carriers in the form of polarons and bipolarons in polyphenylene [8].

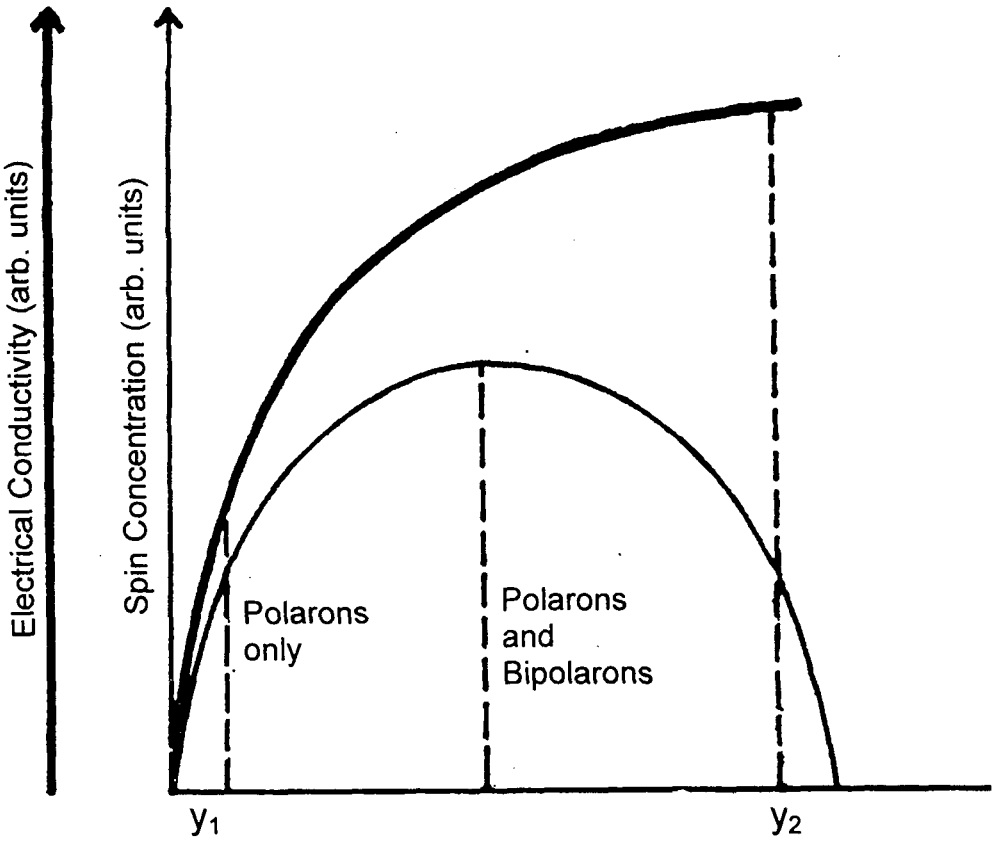


Figure-4. A schematic diagram of the effect of dopant concentration on number of spins and electrical conductivity [8].

Table-2. Comparison of doping behavior of semiconductors, conducting polymers and intercalation compounds [9].

S.No.	Semi-conductors	Conducting polymers	Intercalation Compound
1	Substitutional	Additional	Additional
2	Irreversible	Reversible	Reversible
3	Requires very low Dopant concentrations	Requires quite high dopant concentrations	Requires quite high dopant concentrations
4	Covalent bonds are formed between host and dopant	Interactions bind the host and dopant	Interactions bind the host and dopant
5	Brings about structural changes or lattice expansion	Causes lattice expansion without major structural changes	Causes lattice expansion without major structural changes
6	Host lattice are bonded by covalent bond	Polymer chains are bonded by van der Waal's forces	Host layers are bonded by van der Waal's forces

1.7. De-doping or Undoping

Another important aspect of doping is its reversal, called de-doping or compensation or electrical neutralization of a doped polymer in which, for example, a p-type doped polymer reacts with some reducing agents and regains its insulating state. The de-doping agents, diffuses into polymer matrix and neutralizes the charge of the system by a charge-transfer reaction. The process may involve chemical reactions between the de-doping agent and carbonium ion or/and dopant leading to the neutralization by charge-transfer.

The generally used dedoping agents for p-type doped conjugated polymers include ammonia, water, hydrazine etc. and the chemical reaction for the process may be given by the following equations [8].

$$8\ NH_3 \rightarrow 6\ NH_4^+ + 6\ e^- + N_2 \qquad (10)$$

$$6\ H_2O \rightarrow 4\ H_3O^+ + 4\ e^- + O_2 \qquad (11)$$

$$P^+ + e^- \rightarrow P \qquad (12)$$

De-doping may also be effected by thermal treatment as observed in case of polythiophene. Kinetics of de-doping may be studied by several methods, which could be change in electrical conductivity measurements, x-ray diffraction, optical spectroscopy etc. which may be interpretated into the depletion of the extent of doping [8].

1.8. Role of Doping

Organic chemistry shows that conjugated double bonds behave quite differently from isolated double bonds. As the word indicates, conjugated double bonds act collectively, "knowing" that the next-nearest bond is also double. Huckel's theory and other simple theories predict that π-electrons are delocalized over the entire chain and that the band gap becomes vanishingly small for a long enough chain. One reason for this prediction is the character of a π-molecular orbital, including the p-orbitals of all carbon atoms along the chain of conjugated double bonds. When looking at the distribution of electron density, to which all filled molecular orbitals contribute, the electrons are predicted to be spaced out rather evenly along the entire chain. In other words, all bonds are predicted to be equal. One reason why polyacetylene is a semiconductor and not a conductor is due to that the bonds are not equal: there is a distinct alternation, every second bond having some double-bond character.

The role of dopant is either to remove or to add electrons to the polymer. For example, iodine (I_2) will abstract an electron under the formation of an I_3^- ion. If an electron is removed from the top of the valence band of a semi-conductive polymer, such as polyacetylene or polypyrrole, and vacancy (hole) so created does not delocalize completely, as would be expected from classical band theory. If one imagines that an electron be removed locally from one carbon atom, a radical cation would be obtained.

The radical cation (also called a "polaron") is localized, partly because of coulombic attraction of its counterion (I_3^-), which has

normally a very low mobility, partly because of a local change in the equilibrium geometry of the radical cation relative to the neutral molecule as well as bulkiness.

The mobility of polaron along the polyacetylene chain can be high and charge is carried along as shown in **Figure-5**. Since the counterion (I_3^-) of the positive charge is not very mobile, a high concentration of counterions is required so that the polaron can move in the field of close counterions. This explains the high extent of doping in conducting polymers.

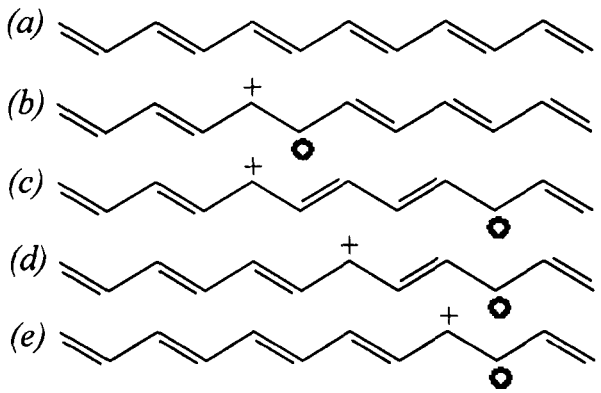


Figure-5. Radical cation ("polaron") formed by removal of an electron on the 5th carbon atom of a undecahexaene chain (a→b). The polaron migration shown in c→e [6].

If a second electron is removed from an already-oxidized section of the polymer, either a second independent polaron may be created or, if it is the unpaired electron of the first polaron that is removed, a bipolaron is formed. The two positive charges of the bipolaron are not independent, but move as pair, like the Cooper pair in the theory of superconductivity. While the polaron, being a radical cation, has a spin of 1/2, the spins of the bipolarons sum to zero. Other difference in the polymer chain, which are important for

conductivity, in polyacetylene are solitary wave defects, "solitons". **Figure-6** shows how a *cis*-polyacetylene chain by undergoing "thermal" isomerization to *trans* structure may create a defect, a stable free radical: this is a neutral soliton which although can propagate along the chain may not itself carry any charge. On the other hand, it may contribute to charge-transfer between different chains.

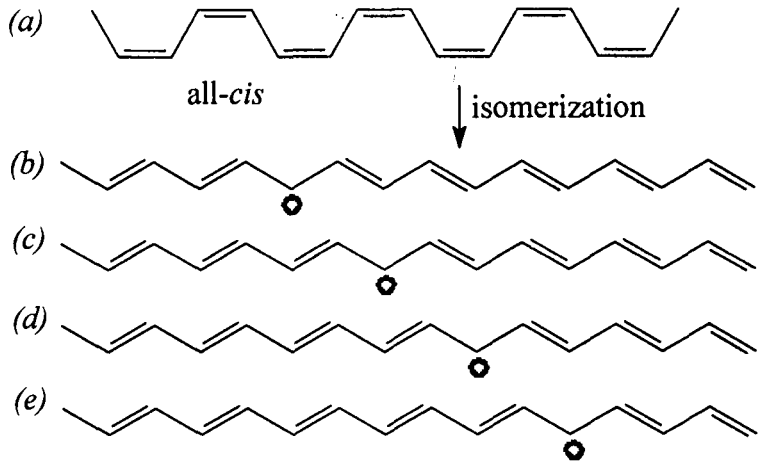


Figure-6. A soliton is created by isomerization of *cis*-polyacetylene (a→b) and moves by pairing to an adjacent electron (b→e). However, generally solitons made by doping are more important than "bond alternation defects" like the one illustrated in this figure [6].

Bulk conductivity in the polymer material is limited by the need for the electrons to jump from one chain to the next, i.e., in molecular terms an intermolecular charge-transfer reaction. It is also limited by macroscopic factors such as bad contacts between different crystalline domains in the material.

One mechanism proposed to account for conductivity by charge-hopping between different polymer chains is "intersoliton

hopping". Here an electron is jumping between localized states on adjacent polymer chains; the role of the soliton is move around and to exchange an electron with a closely located charged soliton, which is localized. The mechanism at work in intersoliton hopping is very similar to that operating in most conducting polymers somewhere in between the metallic state at high doping and the semiconducting state at very low doping. All conjugated polymers do not carry solitons, but polarons can be found in most of them. Charge-transport in polaron-doped polymers occurs via electron transfer between localized states being formed by charge injection on the chain **Figure-7** [6].

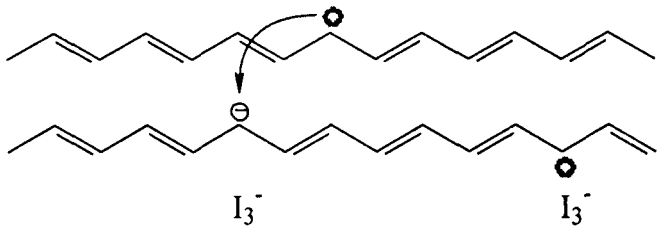


Figure-7. Intersoliton hopping: charged solitons (bottom) are trapped by dopant counterions while neutral solitons (top) are free to move. A neutral soliton on a chain close to one with a charged soliton can interact. The electron hops from one defect to the other [6].

1.9. Photoconduction

Exposure of a semi-conducting material to light or other electromagnetic radiations may produce a temporary increase in the population of free charge carriers and the resulting extra flow of current under the influence of applied field is called photoconduction.

The photon of the radiation can interact with the semi conducting material in a variety of ways to generate charge-carriers. It is very difficult to observe any photoconduction even with UV radiations in ordinary polymers, such as polyethylene (PE) and polyethyleneterephthalate (PET) where the energy of photons is more than the band gap of these polymers. This is a consequence of very short lifetime ($\approx 10^{-9}$) of charge-carriers leading to rapid recombination or deep trapping of the charge-carriers.

One class of organic polymers stands out above all others in its photoconductive efficiency. They are based on vinyl derivatives of certain polynuclear aromatic compounds, such as polyvinylcarbazol [10].

1.10. Degradation and Stability of Electrically Conducting Polymers

The process of deterioration of useful polymer properties involving chemical or photochemical reactions is defined as degradation. There are many external causes of degradation of polymeric materials including heat, light, mechanical stress, oxygen, ozone, moisture, atmospheric pollutants etc. along with the factors effective at the time of processing. Also, the presence of reactive site in the polymer (e.g. superoxide, defects, chemically reactive groups etc.) may degrade the polymer properties with or without combination of external factors [11]

The pristine conjugated polymers have been reported to contain electronic spins leading to the inter- and intra-chain reactions

between these reactive sites which can alter the chemical structure even when they are pure, affecting their dopability and hence the electroactivity. There are two main factors which affect the intrinsic degradation of conjugated polymers viz. reactivity of polymer backbone and the chemical reactivity of dopant ions with polymer etc.

The stability of a polymer may be defined as its ability to retain its useful properties. As electrically conducting polymers are long chain materials with high degree of conjugation as well as unsaturation and with few defects. This implies an electronic structure with filled valence band and empty conduction band. The ionization potential is an important property in ascertaining the stability towards chemical attack of oxygen by charge-transfer process. The extended π-electron overlapping results into lower ionization potential, low enough for oxygen to form charge-transfer complex leading to irreversible puncturing of conjugation.

As the number of conjugated bonds increases, λ_{max} encroaches in to visible region of electromagnetic spectrum, hence, exposure to visible light may also cause irreversible degradation of polymer material through free radicals, bond scission, oxygen attack etc. Electrically conducting polymers may be stabilized by incorporating antioxidants, predoping, encapsulation of device, blending with more stable polymers and synthesizing newer polymer as well as doping agents of better stability by applying new concepts [12].

1.11. Conducting Composites

To meet the demand of materials of improved performance, commercial polymers are always mixed together with various additives of monomeric or polymeric in nature. It is aimed that the additives will act synergistically with the polymer and will meet the combined requirements of a particular application. A polymer composite may be defined as a combination polymer matrix with one or more other materials to avail the advantages of desirable properties of each component. Thus in conducting composites, the polymer matrix acts as a solid adhesive, keeps the conducting components together and provides mechanical strength without any contribution in electrical conduction. A significant amount of the work has been conducted varying the amount of single conductive fillers in a composite material [13-18].

Electrical conductivity in polymers, for example, in natural rubber, was first reported in 1800s when enhanced electrical conductivity was observed in natural rubber on incorporation of carbon black. The use of natural rubber filled with acetylene black began in around 1930s as an antistatic device where it was necessary to prevent the hazard of sparks due to the build up of static electricity. Such composites are enjoying so far a fairly good demand from industry, due to their low cost, lightweight, good mechanical strength and reasonably high electrical conductivity [19].

The electrical conductivity of other polymers can also be increased by the addition of carbon fillers, such as carbon fibers, carbon black and graphite [20-22]. The resulting composites can be

used in applications where metals have typically been the materials of choice [23-26]. The advantages of using these materials include lighting weight, resistance to corrosion, and the ability to be readily adapted to the needs of a specific application. The possible applications for electrically conductive resins include electromagnetic and radio frequency interference (EMI/RFI) shielding for electronic devices, moderately conductive composites for parts such as fuel gauges and electrostatic dissipation (ESD) [27-29].

1.12. Percolation Theory and Electrical Conductivity of Conductive Composites

Electrical conductivity models are often proposed to explain and predict the conductivity behavior of these composites. Development of more accurate models would allow for more efficient materials designed and could therefore reduce costly experimental work, as well as reduce material and production costs through optimized design. These conductivity models typically account for filler volume fraction, constituent conductivity, compatibility of the filler and matrix, filler aspect ratio [30] and properties of the composite structure such as filler orientation [31].

The electrical conductivity of a composite is generally characterized by its dependence on filler volume fraction. The thought is that, as the filler amount in the composite is increased, the fillers particles begin to contact each other and a continuous path is formed through the volume of the sample for electrons to travel. The formation of this conductive network is based on the principles of percolation theory.

The beginning of percolation theory is attributed to Hammersley and Broadbent in 1957 [32]. It was introduced to show how the random properties of a "medium" influence the spread of "fluid" through it. The "fluid" and "medium" can take on several definitions here, including a solute diffusing through a solvent, molecule penetrating a porous solid, a fire spreading through a forest and the flow of electrons through an atomic lattice. This theory was proposed as an alternative to random mechanisms that were typically associated with a flow process within a diffusion process.

One example lay out by Hammersley and Broadbent was that of system of channels, illustrated in **Figure-8**. Each channel divides into two new channels. This random set of dams will thus determine how a fluid will spread through the network of channels. This is a percolation process. This is also known as "bond percolation," as this process can be described as a fluid flowing through interconnected pipes, which are the bonds. The fluid, as shown in the **Figure-9** has a continuous path of bonds to travel through the channel network.

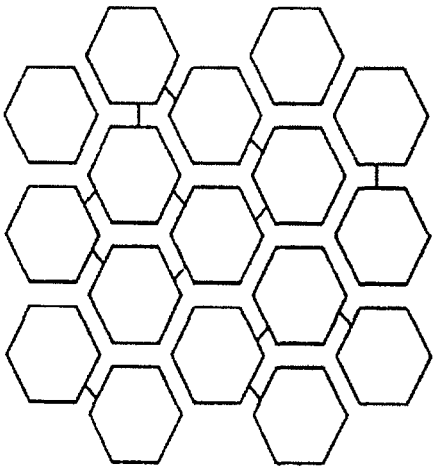


Figure-8. Percolation of a porous medium that is molded as a network of interconnected channels.

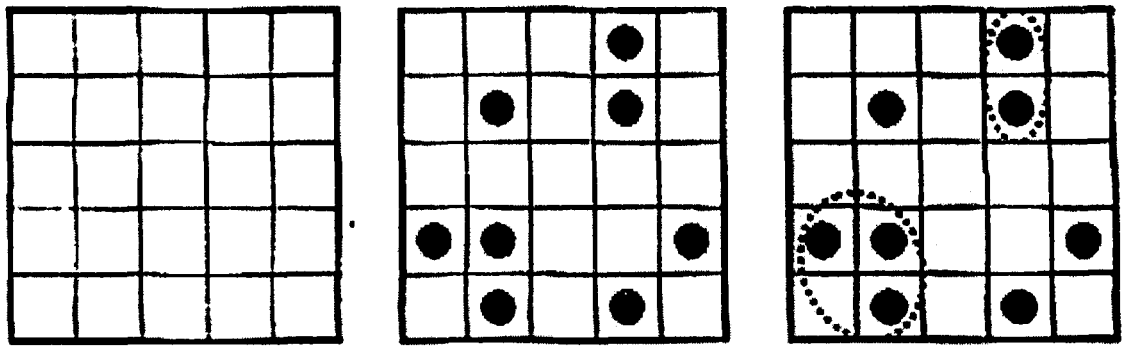


Figure-9. Square lattice with some squares occupied by dots with clusters circled.

Another way to view percolation theory is to visualize a large array of squares, as described by Stauffer [33]. Percolation theory is used to describe the number and properties of these clusters and is defined here as "site percolation." The dots are randomly distributed within the lattice and there is a probability, p, that a site will be occupied by a dot. At a certain probability, there will be a cluster that extends from, in the case of a square lattice, top to bottom and left to right. This cluster is said to be 'percolating' through the system. There is a specific concentration at which this cluster is formed and it is called the 'percolation threshold', denoted by Φ_c.

Stauffer then applied this to forest fires as a simple way to explain the idea of a percolation threshold. The question posed in this example was "how long does a forest take to either penetrate the forest or to be extinguished?" Since it would take a significant number of fires to answer this question with minimal statistical error, the problem was carried out on a computer. A large square lattice similar to that in **Figure-9** will represent the forest. The probability

that an individual square would be occupied by a dot or tree is p, the probability is that a site would be empty. If p = 1, each site would be occupied by a tree.

The trees in the first column on the left of the matrix are allowed to burn whereas the remaining trees are not. It must then be determined if the fire on this side can move through the entire forest to the last column on the right. In order to the fire to spread to, the forest fire is terminated. The lifetime of the forest fire is defined as how many sweeps it takes on each successive column to reach termination. It is as the percolation threshold when this termination occurs at the column and fire has penetrated through the entire forest [34].

An analysis similar to that of the water in the canals can be applied to conductive resins in describing electrical conductivity. The conductive fillers, such as carbon fibers, act as canals for the electrons to flow through.

The electrons are free to flow through the carbon fibers. However, once they reach the end of the fiber, they encounter the polymer matrix, which act as dam, blocking the flow of the electrons. Once enough filler has been added, the carbon fibers begin to come in contact with each other, forming a complete path for the electrons to travel throughout the full volume of the composite. In general, there are three main regions that control the conductivity of filled-polymer composite. The dependence of conductivity on volume fraction is illustrated in **Figure-10** last. At low filler loadings, shown as region **A** in the figure, the conductivity of the composite is still very

close to that of the pure polymer matrix. At some critical loading, the percolation threshold, enough filler has been added so that it begins to form a continuous conductive network through the composite. Following is the percolation threshold, a region that produces significant increases in conductivity with very little increases in filler amount, as displayed by region **B**. After this region of drastic increase, the conductivity again levels off and approaches that of the filler material. This occurs because the conductivity network through the sample is complete and the electrons are following the path created by the connected filler particles. This is depicted in area **C** of **Figure-10**.

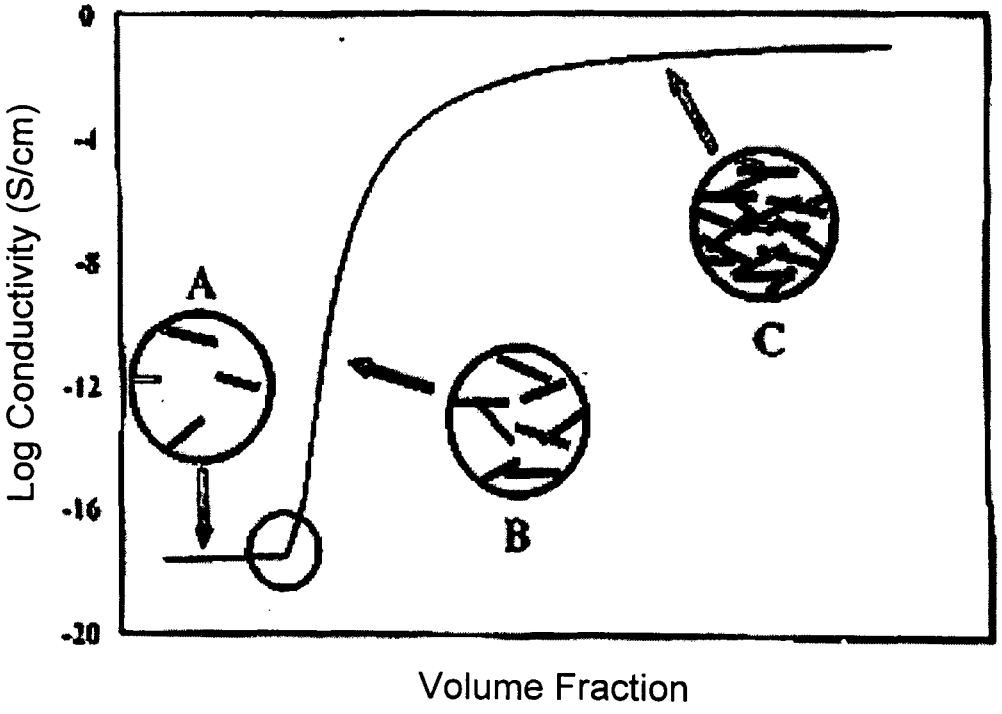


Figure-10. Dependence of Electrical Conductivity on Filler Volume Fraction.

There are several factors that can have a significant effect on where the percolation threshold lies and the plateau conductivity level. In addition, various models have been proposed in an effort to predict the electrical conductivity behavior of composite based on numerous factors. The majority of the models are based on the calculations on filler volume fraction while other factors can affect the conductivity of the composites. The same factors can also affect the volume fraction at which the percolation threshold occurs.

1.13. Factors Affecting Electrical Conductivity of Composite Materials

The properties of the filler play a significant role in determining the conductivity of the composite. Carbon when used as filler, comes in many different forms, from small carbon particles to graphite fibers and the conductivity of each is different. Typical electrical conductivity values for other materials are 10^2 S/cm for electrically conductive carbon black, 10^3 S/cm for polyacrylonitrile (PAN)-based, 10^4 S/cm for pitch-based carbon fibers and 10^5 S/cm for graphite. The value for filler conductivity will be the upper limit for the electrical conductivity of the composite.

Other filler properties, such as particle size, can also have an effect on the electrical conductivity. It has been shown that for spherical particles, smaller particle size will lower the percolation threshold [35]. It has also been shown that an aspect ratio (ratio of length to diameter, l/d) greater than one, as well as a broader range of aspect ratios will lower the percolation threshold [36-38]. Another important item for consideration is the method by which the composites are made and subsequently molded in to components.

There are several studies that show the effects that filler orientation has on the electrical conductivity of composites and how this effect can be quantified [39-44]. Extrusion and injection molding of a composite can align fillers that have an aspect ratio greater than one in a certain direction due to the flow through the nozzle of the machine and the mold. This alignment will produce anisotropic conductivity within the sample, meaning that conductivity will be greater in one direction than in other. Compression molded samples will also display an effect of filler orientation on electrical conductivity.

Weber and Kamal [45] found that injection molded samples had a 33.6° angle of orientation while the compression molded samples with the fillers at a 45.2° angle. Deviation from a 45° angle is the evidence that there has been alignment of the fillers.

The surface properties of the filler and polymer also have a significant effect on the conductivity and the percolation threshold of the composites. The surface free energies of the filler and matrix will influence the interaction between two materials, and how well the polymer wets the surface of the filler can be quantified by the difference between the surface energies of the two materials. Mamunya showed that the smaller difference between the surface energies of the two lead to better wetting of the filler by the polymer [46]. Therefore, better wetting of the filler can improve its dispersion within the matrix material. While this can increase the percolation threshold of the composite, it can also improve the overall conductivity of the composite. In general, a smaller difference

between the surface energy of the filler and polymer is desirable to obtain high electrical conductivity composites.

1.14. Conductivity of Various Composite Materials

By adding conducting fillers to the polymers, materials can be designed with specific properties tailored to each application. For composites materials to be used for conductive applications, the material should have an electrical conductivity in the range of 10^{-12} and 10^{-8} S/cm for ESD applications, 10^{-8} and 10^{-2} S/cm for moderately conductive applications and 10^{-2} S/cm and higher for shielding applications [47-49].

There are numerous examples where conductive fillers have been added to plastics to produce conductive composites. Metal fibers/particles, including aluminum, steel, iron, copper and nickel coated glass fibers have been used [50,51]. Carbon black and carbon fibers have also been used to improve the conductivity of polymers [52]. Carbon black fillers have been successfully used to improve electrical conductivity, but these materials often have no effect on the thermal conductivity. Carbon fibers, on the other hand, have performed well to improve the thermal and electrical conductivities.

Demand for conductive resins in the U.S. in 1995 was 221 million lbs. Conductive polymer demand in the US is projected to grow 6.1 percent annually to 565 million pounds. The growth in conductive resin demand is due to stringent regulations on electronic noise and the increased sensitivity of electronic parts and

components. For example, increased demand for high-speed electronic devices combined with miniaturization trends, stimulates the demand for EMRI/RFI shielding and ESD protection. Smaller, more densely packed electronic components produce more electronic noise and, therefore, require more EMI/RFI shielding and are more susceptible to static discharges.

Additional conductive resin demand is driven by high levels of static electricity generated by moving parts, such as rollers in copiers and printers, which must be controlled for proper operation.

1.15. Electroluminescent Polymers-Second-Generation Conductive Polymers

Since the first report of metallic conductivities in "doped" polyacetylene in 1977, the science of conductive polymers has advanced rapidly in various directions [53-55]. More recently, as high purity polymers have become available, a range of semiconductor devices have been investigated. These include normal transistors and field-effect transistors (FETs) and photodiodes and light-emitting diodes (LEDs). In particular, polymers LEDs now show attractive characteristics, including efficient light generation with great potential for commercialization. Again, the principal interest in polymers is in their rapid and low-cost processing from polymer solutions.

Like the conductive polymers, the semi-conductive polymers obtain their properties from their conduction-molecular orbitals and valence molecular orbitals, i.e. bonding π-orbitals and antibonding π^*orbitals, respectively.

In electrochemical light emitting cells, the semi-conductive polymer could be surrounded asymmetrically with a hole-injecting electrode (usually ITO) on one side and a low work function, electron injecting metal contact (e.g., aluminum, magnesium or calcium) on the other side. The emission of light is then the result of radiative charge carrier recombination in the polymer as electrons from one side and holes from the other recombine.

Electroluminescence from conjugated polymers was first reported in 1990 [54]. Poly(p-phenylenevinylene) PPV was used as the single semi-conductor layer. In light emitting polymer diode, the semi-conductive polymer could be surrounded symmetrically with a hole-injecting electrode (transparent ITO) on one side and a low work function, electron-injecting metal contact (e.g., aluminum, magnesium or calcium) on the other side. With proper bias, electrons and holes are injected, which meet in bulk of the polymer film. The emission of light is then the result of radiative charge carrier recombination in the polymer film. PPV has an energy gap between the LUMO (π) and HOMO (π^*) orbitals of about 2.5 eV and thus produces yellow-green luminescence, with the same emission spectrum as that produced by normal photo excitation of conjugated polymer. Much higher efficiencies have been reported for LED polymer diodes in which a layer of poly(dioxyethylenethienylene) doped with styrene sulphonic acid or polyaniline:hydrochloride is inserted between the indium-tin oxide and the emissive polymer layers.

1.16. Diffusion in Conducting Polymers

Mirebeau [56] produced conductive polypyrrole films on stainless steel electrodes in an electrochemical cell containing propylene carbonate and lithium tetrafluoroborate ($LiBF_4$). He measured the diffusion coefficient of ClO_4^- in an as-prepared PPy-ClO_4 for undoping and doping by a potentiostatic method in the temperature range of 240 to 320 K. A diffusion coefficient of 5.0×10^{-12} cm^2s^{-1} was estimated at 298 K. Mirebeau also estimated the activation energy of diffusion to be 30 $kJmol^{-1}$ (0.31 eV) from an Arrhenius plot which could approximately be expressed by the equation, $D = 6.8 \times 10^{-7} \exp^{(-0.31eV/kT)}$.

Gennies et al. [57] have shown that the apparent diffusion coefficient into and out of PPy-ClO_4 is a function of salt ($LiClO_4$) concentration in the electrolyte. The electrochemical oxidation and reduction follow the Nernstian relation and a value of 6.0×10^{-10} cm^2s^{-1} has been reported for apparent diffusion coefficient at 298 K in a 0.5M $LiClO_4$/acetonitrile solution. The $D_{apparent}$ follows an inverted U shaped relationship with the variation in $LiClO_4$ concentration in the electrolyte and the value for doping are slightly lower than that for undoping processes at 298 K. A model for time-dependence of concentration relaxation of holes S^+, Li^+ and ClO_4^- has been suggested for diffusion during doping and undoping processes. They proposed that the diffusion involves the concentration relaxation of all three species simultaneously to maintain electroneutrality in the system.

The reported values of diffusion coefficients for small dopants vary from 10^{-5} to 10^{-18} cm^2s^{-1} into Shirakawa polyacetylene [58,59],

which possesses highly crystalline and fibriller structure of very high surface area [60]. However, for "Durham" polyacetylene, which gives very dense and amorphous films, the diffusion coefficients range from 10^{-14} to 10^{-13} cm^2s^{-1} for Li^+, Na^+, ClO_4^-, BF_4^-, I_2 and AsF_5 [61].

Abalyaeva et al. [62] used as a combination of voltabsorbometry and chronoabsorbometry to estimate the coefficient of BF_4^- diffusion in to 0.49 μm thick film of polyparaphenylene produced by vacuum evaporation and a value of 5.0×10^{-9} cm^2s^{-1} has been reported.

Stamm [63] estimated a value of 3.0×10^{-6} cm^2s^{-1} for AsF_5 diffusion into oriented fibers of polyparaphenylene produced by solid-state extrusion technique.

Chapter-Two

Review of Literature

CHAPTER-2

2. REVIEW OF LITERATURE

2.1. Introduction

The Royal Swedish Academy of science to awarded the Nobel Prize in Chemistry for the year 2000 to three scientists who have revolutionized the development of Electrically Conductive Polymers. Professor Alan J. Heeger at the University of California at Santa Barbara (USA) Professor Alan G. MacDiarmid of the University of Pennsylvania (USA) and Professor Hideki Shirakawa at the University of Tsukuba (Japan) were rewarded "*for the discovery and development of Electrically Conductive Polymers*".

2.2. Conductive Polymers – Surprising Discovery

We are used to polymers i.e., plastics, in certain sense being somehow the opposite of metals. They are insulators, as they do not conduct electricity. Electric wires are coated with polymers to protect them – and us – from short circuits [1]. Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have changed this view with their discovery that a polymer, polyacetylene, can be made conductive almost like a metal.

Polyacetylene was known as a black powder when it was prepared in 1974 as a silvery film by Shirakawa and co-workers from acetylene, using a Ziegler-Natta catalyst. But despite its metallic

appearance, it was not a conductor. In 1977, however, Shirakawa, MacDiarmid and Heeger discovered that oxidation with chlorine, bromine or iodine made polyacetylene films 10^9 times more conductive than they were originally [2].

2.3. Conductive Polymers – The Story

2.3.1. Polyacetylenes

Polyacetylene (**Figure-11**) was the conductive polymer that actually launched this new field of research [3-5]. For the details of its history see the excellent review articles by Feast et al [6] and by M.G. Kanatzidis [7].

Natta and co-workers prepared polyacetylene in 1958 by polymerizing acetylene in hexane using $Et_3Al/Ti(OPr)_4$ (Et = ethyl and Pr = propyl) as catalyst [8]. Though the resulting material was highly crystalline and of regular structure, it was a black air-sensitive, infusible and insoluble powder. Ziegler-Natta polymerization was developed for polymerizing alkenes such as ethylene by inserting an unsaturated molecule in to the carbon-titanium bond of the growing macromolecule. It depends greatly on the activity of the choice of catalyst system. In the early 1970's, Shirakawa and coworkers adapted the method to make well-defined films of polyacetylene [9,10].

Figure-11. Chemical structure of cis-polyacetylene.

A major discovery by Shirakawa was that this polymerization could be effected at the surface of a concentrated solution of the catalyst system in an inert solvent. The synthetic procedure involved adding $Ti(OBu)_4$ and then Et_3Al to a small volume of toluene under an inert atmosphere. The solution was allowed to 20°C for 45 minutes and was then cooled to –78°C. The reaction vessel was evacuated and acetylene gas introduced and allowed to react with a film of the catalyst, which had already formed on the wall of reaction vessel. A film of polyacetylene immediately formed there [3]. The reaction was controlled by evacuating unreacted acetylene gas. This procedure produced a copper-colored film of all *cis*-polyacetylene with a *cis* content of about 95 percent. Shirakawa's procedure also allowed silvery all *trans*-polyacetylene to be formed by performing the reaction in n-hexadecane at 150°C. However, its conductivity was relatively modest: *cis*-polyacetylene 10^{-8}-10^{-7} S/m and *trans*-polyacetylene 10^{-3}-10^{-2} S/m.

In 1997, Professors Alan J. Heeger and Alan MacDiarmid collaborated to study the metallic properties of a covalent inorganic polymer, (SN)x . They shifted their attention to polyacetylene after MacDiarmid met Shirakawa in Tokyo. During a visit at the University of Pennsylvania, Shirakawa refined the polymerization of polyacetylene. With his experience from the (SN)x materials, MacDiarmid wanted to modify the polyacetylene by iodine treatment. Shirakawa and Ikeda had previously noted the treating silvery polyacetylene films with bromine or chlorine decreased the infrared transmission without altering the color. MacDiarmid now turned to

Heeger in whose laboratory a conductivity of $3x10^{-3}$ S/cm was measured for iodine-modified *trans*-polyacetylene, an increase of seven orders of magnitude over the undoped materiai.

Exciting experiments followed. Shirakawa could now control the ratio of *cis/trans* double bonds. *Cis*-polyacetylene doping resulted in even higher conductivities (**Figure-12**). The iodine may first have isomerized the polymer to all *trans*-materials, which then underwent efficient (defect-free) doping so that the overall degree of orientation in the doped polyacetylene was greater. Doping of *cis*-polyacetylene with AsF_5 resulted in an increase of conductivity by factor of 10^{11}. The high conductivity found by Heeger, MacDiarmid and Shirakawa clearly opened up the field of "Plastic Electronics".

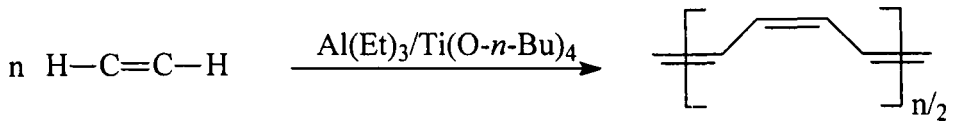


Figure-12. Shirakawa's route of polyacetylene synthesis.

In 1980, Ekelmann et al. [11] noted that powder polyacetylene specimens prepared by traditional methods possessed properties which were essentially the same as those of the material produced by Shirakawa's method. Such powders could be suspended in an inert solvent and application of the suspension to the suitable substrate followed by evaporation of the solvent gave thin films of polyacetylene. They also showed that solid specimens of almost any desired size could be prepared by molding polyacetylene powders. Later, Ekelmann et al. [12] discovered that the best results are obtained using $Co(NO_3)/NaBH_4$ as the initiator system. Systems of

this type containing salts and complexes of group (VIII) metals together with a hydride reductant were first used by Luttinger [13] twenty years earlier. In a typical experimental procedure, ethanol is saturated with gaseous acetylene and sodium borohydride followed by cobalt nitrate, are added. After several hours at room temperature to -30°C, the formation of a predominantly *cis* structure is favored [12].

The main advantage of Luttinger's catalyst over that developed by Shirakawa is that it allows the polymerization reaction to be carried out even in the presence of water and oxygen (**Figure-13**). Frohner and Wuckl [14] studied the kinetics of the reaction and found that the initial polymerization rate is high and that the polyacetylene yield is proportional to the concentration of the cobalt species. Furthermore, the same workers observed that decreasing the reaction temperature results in an increase in polymer yield and in crystallinity.

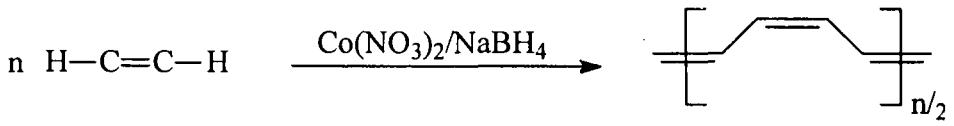


Figure-13. Luttinger's route of polyacetylene synthesis.

2.3.2. Polyphenylenes

The synthetic routes employed for the preparation of polyphenylenes include mainly: oxidative coupling, organometallic coupling, dehydrogenation of polycyclohexylenes and cycloaddition reaction. These, together with the other methods available for the

synthesis of polyphenylenes, are discussed in the forth-coming sections.

2.3.2.1. *Oxidative coupling*

The most commonly employed method for the preparation of polyphenylenes involves the oxidative coupling of substituted and unsubstituted benzenes via treatment with a Lewis acid catalyst/oxidant system. In 1963, Kovacic and Kyriakis [15] synthesized poly(p-phenylene) by stirring benzene, anhydrous $AlCl_3$ and anhydrous $CuCl_2$ for 2h at temperatures between 25°C and 35°C. The reaction is believed to involve an initial one-electron oxidation of benzene to its radical cation, followed by reaction of the radical cation with several benzene molecules to give oligomeric radical cation. A second one-electron oxidation followed by loss of two protons aromatization of the dihydrostructures by $CuCl_2$ yields the polymer [16].

A number of catalyst/oxidant systems have been employed for conversion of benzene to polyphenylenes. These include Cu^{2+} and Ru^{3+} ion-exchanged montmorillonite clays [17,18] and AsF_3/AsF_5 [19]. The structural features and physical properties of the polymer prepared via oxidative polymerization depend to a large extent on the nature of the reagents [20]. Thus, it has been claimed that polyphenylenes with *ortho* linkages can be obtained from the oxidative polymerization of monosubstituted benzene (toluene, chlorobenzene) under conditions analogous to those employed for the preparation of poly(p-phenylene) [20]. Polyphenylenes linked at the *meta* position are in general synthesized by treatment of m-

terphenyl or mixture of the *m*-terphenyl and biphenyl with anhydrous $AlCl_3/CuCl_2$ at elevated temperatures (85°C and 180°C) [21,22]. Polymers substituted in the *para* position are in general more difficult to process than the *ortho* and *meta* substituted analogues. Oxidation in liquid SO_2 at –75°C or concentrated sulfuric acid in the presence

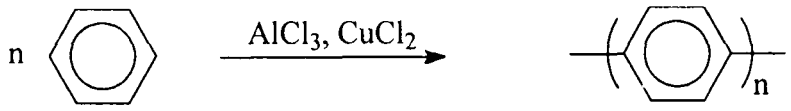


Figure-14. Poly(p-phenylene) synthesis by oxidative coupling.

of $AlCl_3$ are claimed to result in the efficient formation of homogeneous poly(*para*-phenylene), which is almost completely amorphous (**Figure-14**) [23]. Highly crystalline films of this polymer can be deposited from benzene in concentrated sulfuric acid emulsion [24]. An alternative means for the synthesis of polyphenylenes involve the anodic electrochemical oxidation of benzene or biphenyl in liquid sulfur dioxide on an appropriate electrode. The reaction yields passivating films if quaternary ammonium perchlorate is used as electrolyte or conductive dendretic deposits are formed if quaternary ammonium tetrafluoroborate is employed [25]. In both the cases, the polymer formed is reported to be linked at the *para* position but contains variable amounts of oxygen as phenolic groups. The electrochemical polymerization of benzene in nitromethane with aluminium chloride and water or an amine as additive results in the deposition of black polyphenylene on a platinum electrode [26]. Free standing polyphenylene films containing *ortho*, *para* and *meta* links are obtained if the electrochemical oxidation of benzene is carried out in a two phase

HF/benzene system [27]. The anodic oxidation of benzene in nitrobenzene solution with $CuCl_2$ and $LiAsF_6$ results in the formation of flexible electrically conducting films of poly(*p*-phenylene) [28,29] as does the anodic oxidation of benzene in the presence of $BF_3.OEt_2$ [30]. The yields of the polymers prepared by this method are restricted by the area of anode irrespective of whether the reaction is carried out in nitrobenzene or in the bulk [31].

2.3.2.2. *Organometallic coupling*

Ullmann and Wourtz-Fittig type reactions have been utilized for the synthesis of polyphenylene oligomers but these methods cannot be applied to the synthesis of polymers since the yields are comparatively very low [32]. The preparation of polyphenylenes via the coupling of Grignard reagents has proved more suitable [32]. Thus, the coupling of mono-Grignard reagent of dihalobenzene (**Figure-15**) in presence of organometallic or organic promoters [33,34] has been used for the synthesis of a range of *para* and *meta* substituted polyphenylenes [35-37]. However, the combination of lithiated anthracene and anthraquinone species is reported to be the most efficient method for the synthesis of polyanthrylene [38-40].

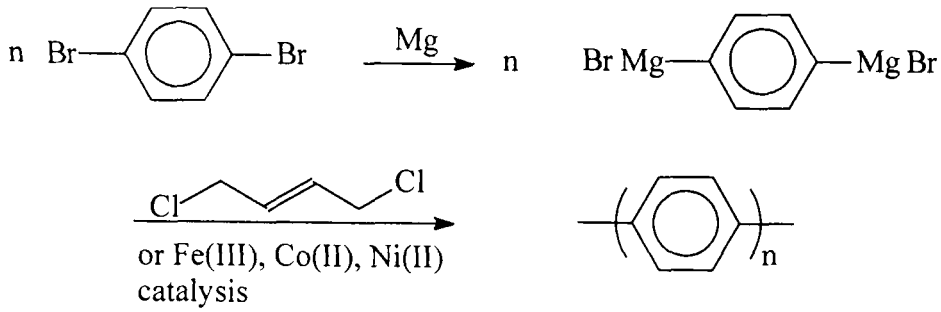


Figure-15. Poly(p-phenylene) synthesis by Grignard's route.

2.3.3. Polyanilines

Polyaniline (**Figure-16**) also known as 'aniline black', was first prepared in 1834 and has been the subject of intensive research ever since [41]. In the 1980s, the conducting properties of polyaniline were recognized and the number of papers dealing with this conducting polymer grew rapidly. The main reasons for this growth, besides the scientific interest, are the low cost of aniline, the relatively easy production process and the stability of the conducting forms.

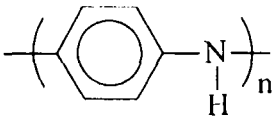


Figure-16. Chemical structure of polyaniline.

2.3.3.1. *Synthesis of polyaniline*

Oxidation of aniline is the most widely employed synthetic route to polyaniline and can be performed either electrochemically or chemically. The reaction is usually carried out in the acidic media. The electrochemical method was originally developed by Lethby as a test for the determination of small quantities of aniline [42]. The method has been improved ever since [43-45] and has also been applied to alkyl [46,47], alkoxy [48] and dimethoxy [49] substituted anilines, the later exhibiting conductivity comparable to that of unsubstituted polyaniline.

Chemical oxidation is usually carried out in the acidic aqueous environments with an oxidizing agent such as ammonium persulfate

[50], but has also been performed in chloroform using tetrabutyl ammonium periodate [51]. Alkyl [46] and alkoxy [48] substituted polyanilines have also been prepared utilizing this chemical method.

It has been stated that cross-linking occurs in polyaniline during the electrochemical synthesis due to the potential applied [52]. However, non-oxidatively synthesized polyaniline, exhibiting the similar properties, has a fully linear structure [53]. Cross-linking in polyaniline can also be accomplished when the emeraldine base is heated up to 300°C [54].

2.3.3.2. *Properties of polyaniline*

Polyaniline can occur in a number of well-defined different oxidation states [54], each with its own name as originally attributed by Green and Woodhead (**Figure-17**) [55].

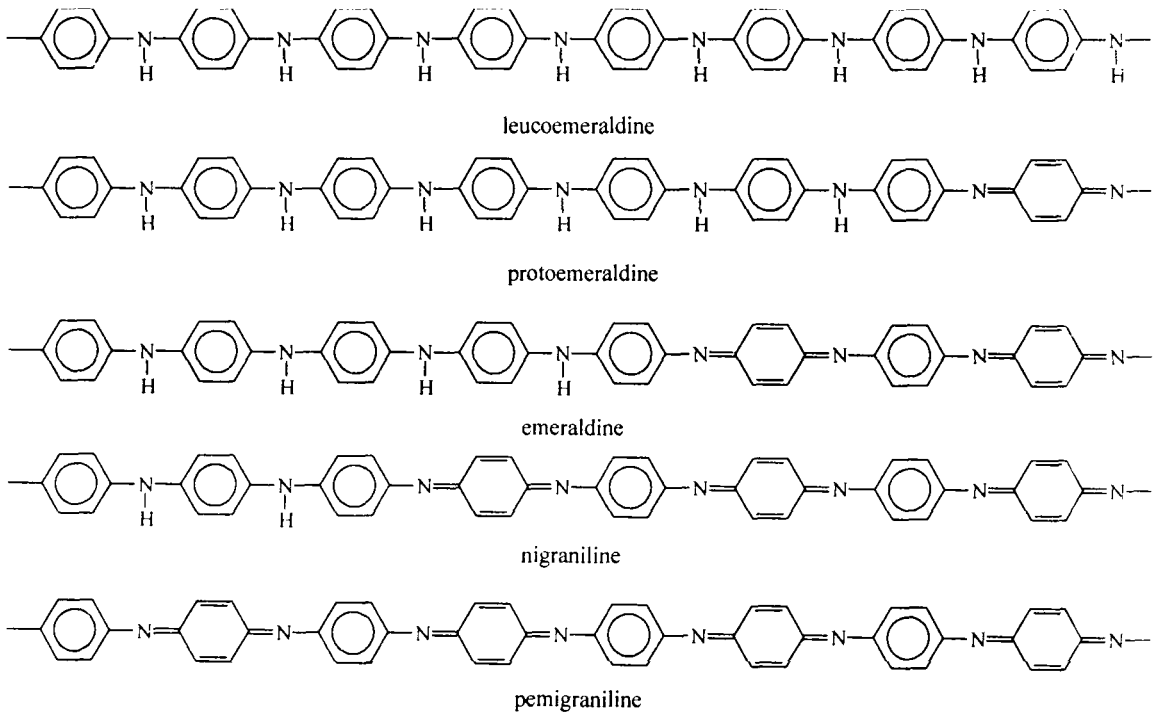


Figure-17. Different oxidation states of polyaniline.

The different states range from the fully reduced leucoemeraldine via protoemeraldine, emeraldine and nigraniline to the fully oxidized pernigraniline.

Unlike in mostly other polyaromatics, the fully oxidized state in polyaniline is not conducting as a matter of fact none of the above-described states are conducting. Polyaniline becomes conducting when the moderately oxidized states, in particular the emeraldine base, are protonated and charge carriers are generated. It is this process, generally called 'protonic acid doping' [46], which makes polyaniline so unique; no electrons have to be added to or removed from the insulating material to make it conducting. The different oxidation states of polyaniline can also be generated by doping with oxidants such as iodine, but the resulting conductivity is lower than that obtained via protonic acid doping [56-58]. The conduction mechanism is believed to involve polaronic carriers; the protonated emeraldine (**Figure-18**) consists of a delocalized poly(semiquinone radical cation).

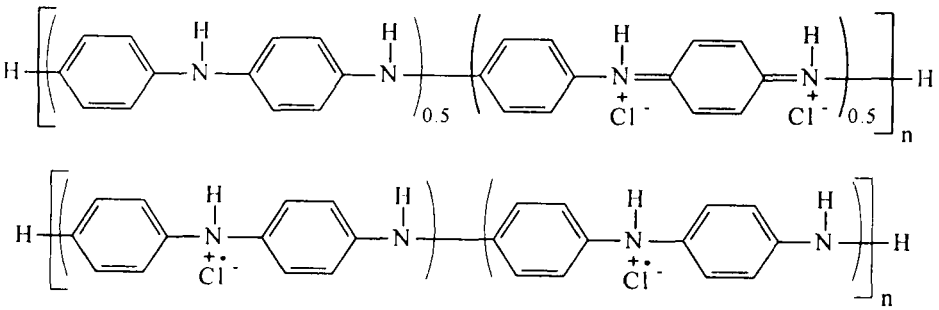


Figure-18. Chemical structure of emeraldine salt.

The conductivity is affected by the water content as completely dry samples are five times less conductive than samples containing some water [50]. The emeraldine base is soluble in N-methyl-pyrrolidone [59], but protonated polyaniline is insoluble in organic solvents and only soluble in aqueous acids. Substitution of aniline monomer with alkyl or alkoxy groups improves the solubility in organic solvents but has a negative influence on the conductivity [60-62]. The position of the substituent also has an influence on the polymerization. The *ortho* and *meta* isomers give the same polymer, but the reactivity of the *meta* isomer is considerably lower, resulting in a lower yield. Self-doped polyaniline, containing sulfonic acid substituents, has been synthesized by sulfonation of the emeraldine base [63].

Although no data are available concerning the health risks of polyaniline, the possible presence of benzidine moieties, which are well-known carcinogens, suggests careful manipulation of both, aniline and its polymers.

2.3.4. Polythiophenes

Polythiophene (**Figure-19**) synthesis was described in 1883 when the purification of thiophene with sulfuric acid yielded a dark insoluble material [64]. However, it was not until the early 1980s that any well-defined polymeric material was obtained. After the first reports of a controlled synthesis by Yamamoto [65] and Lin [66], using the Grignard-type coupling of 2,5-dibromothiophene, a vast number of

articles concerning the synthesis and properties of polythiophene have been published.

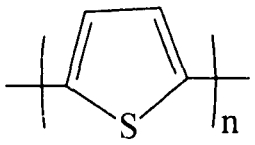


Figure-19. Chemical structure of polythiophene.

Extended π-conjugation in polythiophene is only possible in polymers with perfectly 2,5-linked repeating units; however, 2,4- and 2,3-couplings as well as hydrogenated thiophene units can also be found in the polymers [67]. These structural defects interrupt the conjugation and, as a result, will impair the development of properties related to conductivity and nonlinear optics.

Polythiophenes, like many other linear polyaromatic compounds, are insoluble in organic solvents due to their rigid backbone. This lack of solubility and processsibility, as well as problems related to the characterization of polythiophenes, has been overcome by the introduction of flexible side chains at the 3- and/or 4-position. Appropriate solubility in common organic solvents has been achieved with an alkyl side chain of more than four carbon atoms at every repeating unit [68]. Longer alkyl side chains are required in the case of co-polymers with less than one side chain per repeating unit. With the introduction of substituents at the 3-position of polythiophenes, a number of different regioisomers are possible, namely head–to-tail (HT), head-to-head (HH) and random configurations (**Figure-20**) [69,70].

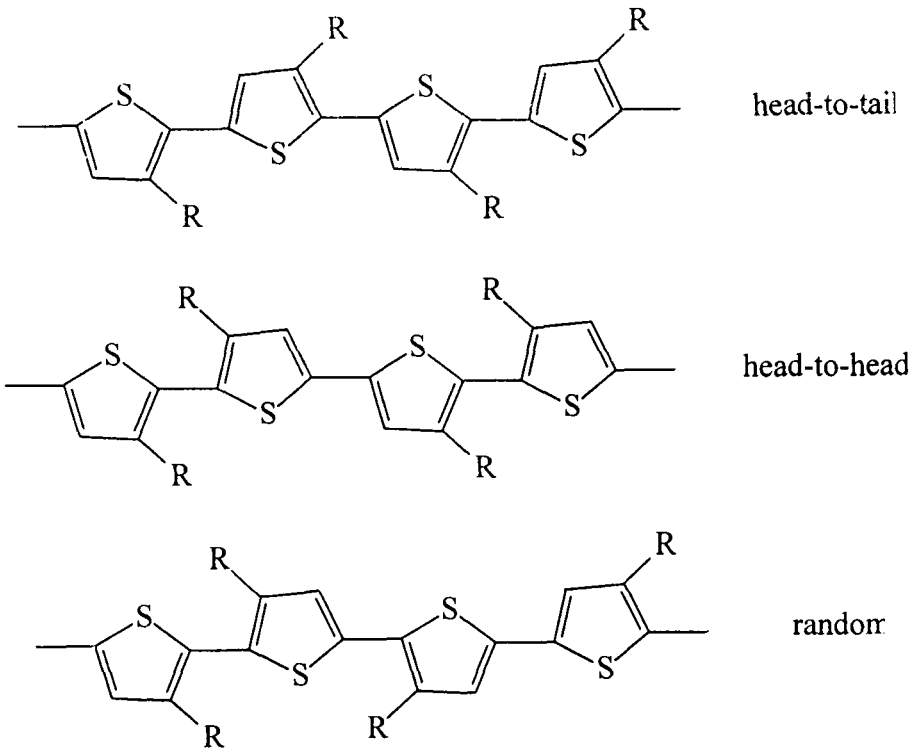


Figure-20. Different regioisomers in polythiophene.

Head-to-head coupling of alkyl groups is sterically unfavorable for coplanarity and hence causes a significant loss of conjugation, however, head-to-tail couplings do not limit conjugation. The significant difference in coplanarity between HH and HT couplings shows the subtleties in the trade off between resonance energy and steric hindrance in substituted polyheterocycles. Studies on regioregular polythiophenes, recently accessible via a number of elegant routes, have shown that the crystallinity increases with regioregularity and that the possibility of side-chain crystallinity is essential for the development of optimal properties. In the case of regiorandom polymers, the optimal chain length for properties like conductivity and optical nonlinearities has been determined to be in the range of seven to nine carbon atoms [71]. The conductivity of doped regioregular polythiophenes with an *n*-dodecyl side chain at

the 3-position surpasses that of polymers with an *n*-octyl side chain [72]. Even self-assembly in thin films of regioregular 3-substituted polythiophenes has been observed.

In addition to improved solubility and crystallinity, the introduction of side chains in the 3- and/or 4-position also decreases the probability of α-β couplings, since at least one of the β positions is already occupied [73,74], 3,4-Dialkyl substitution in monomers results in a significant loss of coplanarity [75]. While in 3,4-dialakoxy and 3-alkyl-4-alkoxy polythiophenes, the presence of an oxygen atom attached to the thiophene unit is enough to decrease steric hindrance and limit the loss of conjugation [76]. An unexpectedly high regioregularity was found in the polymerization of 3-methyl-4-alkoxythiophene [77].

2.3.4.1. *Electrochemical synthesis of polythiophenes*

Since the first reports by Diaz [78], the synthesis of polythiophenes by electrochemical oxidation has been widely used. Although the mechanism is not fully understood, it is proposed that the polymerization proceed via the coupling of two radical cations, formed by the oxidation of the monomer as out line in **Figure-21** [79]. Aromatization of the bithiophene intermediate is the driving force for the transformation of the dihydrodimer. The dimer, having a lower oxidation potential than the monomer, is readily oxidized and undergoes further coupling. The polymer is deposited in its oxidized conducting form on to the electrode, allowing the polymerization to proceed. This method has the advantage that homogeneous and stable films are formed in this polymerization. These films are

characterized by optical and electrochemical method. The electrochemical polymerization has been applied for the synthesis of unsubstituted polythiophene [80,81] and 3-substituted polythiophenes including poly(3-methylthiophene) [82], poly (3-ethylthiophene) [83] and number of different soluble poly(3-alkylthiphenes) [84,85]. However, in all the cases reported so far, the polymers obtained possess a regiorandom structure.

The electrochemical polymerization of substituted thiophenes has also been used to synthesize a variety of functional polymers. Oxygen containing substituents on the 3-position of thiophenes have been used, including methoxy [86] and polyether substituents [87], leading to the materials with conductivities as high as 1000 S/cm. A highly transparent conducting polymer has been obtained from the electrochemical polymerization of 3,4-ethylenedioxythiophene [88].

Similarly, polyfluoroalkyl substituted polythiophenes can be synthesized [89], while water soluble, self-doped polythiophenes have been prepared by the introduction of ionic groups in the side chain [90-93] .

Thiophene oligomers such as bithiophenes [94] and terthiophenes possess lower oxidation potentials than the thiophene monomers (1.05V, 1.13V, and 2.07V vs. SCE for terthiophene, bithiophene and thiophene respectively) [95]. They are, therefore, more suitable for the electrochemical polymerization since this lowers the oxidation potential and decreases the risk of over oxidation. Also, 2,5-disilyl substituted thiophenes have been

polymerized electrochemically with concomitant elimination of the silyl substituents [96].

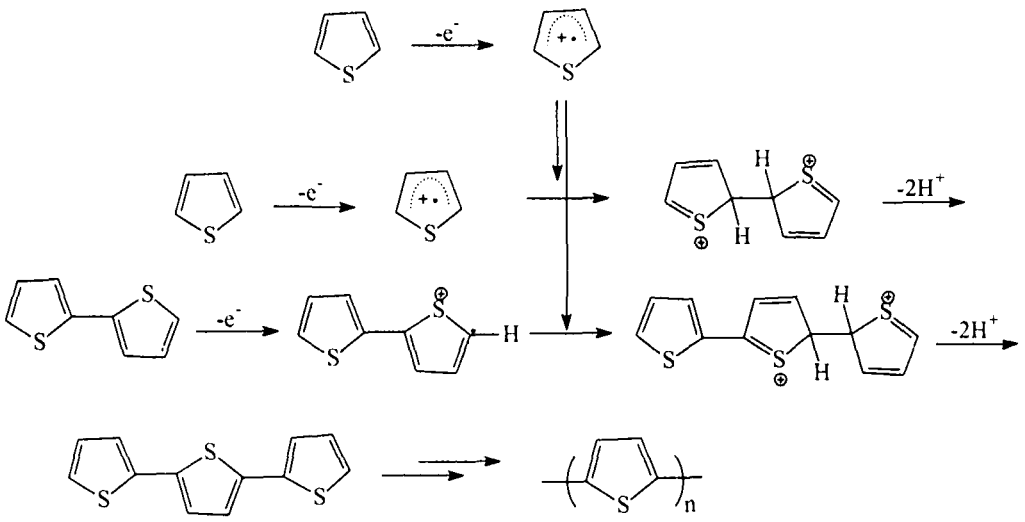


Figure-21. Electrochemical polymerization of thiophene.

2.3.5. Polypyrroles

The synthesis of polypyrrole (**Figure-22**) that included a description of the conducting properties of the products was published in 1968 [97]. The electrochemical oxidation of pyrrole in 0.1N sulfuric acid yielded a black conducting film. Improvements by using organic solvents and different electrolytes have made the electrochemical method, the most commonly employed polymerization technique [98,99]. The mechanism of the electrochemical polymerization is similar to that of thiophene.

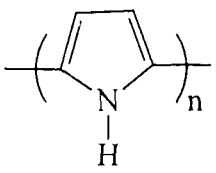


Figure-22. Polypyrrole.

Oxidized polypyrrole is stable under ambient conditions and up to temperatures exceeding 300°C. The neutral form of polypyrrole, on the other hand, has not been isolated and characterized, due to extreme susceptibility to oxidation (-0.02V vs. SCE).

The electrochemical route of polypyrrole provides good quality films. The counter ion have considerable influence on the conductivity and mechanical properties [100], and thus changing the counter ion from oxalate to perchlorate increases the conductivity [101,102]. Commercially available polypyrrole films with tosylate as counterion exhibit a conductivity of 15 Scm^{-1}. The stability of the film under ambient conditions is extremely good, a decrease in conductivity of less than 15% per year has been reported [103]. Alkylsulfonates and phosphates have also been used as electrolytes [104], while processible polymer blends have been formed using sulfonated polystyrenes as counterions [105].

Oxidation with chemical oxidizing agents (such as sulfuric acid [106], bromine and iodine [107], copper II perchlorate [108] and iron trichloride [109]) of a neutral polypyrrole film increases conductivity compared to that of the electrochemicaly oxidized material [110]. 2,2'-Bipyrrole has been used as monomer in the chemical oxidative polymerization, but the properties of the product are similar to that of the polymer prepared directly from pyrrole [111].

Soluble polypyrroles can be prepared by the introduction of flexible side chains [112-114]. In contrast with the progress made in the synthesis of regioregular 3-substituted polythiophenes, all 3-

substituted polypyrroles reported so far are synthesized in a regiorandom fashion. 3-Alkylpyrroles, the monomers in the electrochemical polymerization, have been synthesized via Friedal-Craft's acylation of N-protected pyrrole, followed by Clemenson reduction [115-117].

Substitution at nitrogen also affords soluble polymers. However, the conductivity reduced drastically due to strong steric interactions of this substituent at nitrogen and hydrogen at the 3- and 4-positions of the adjacent pyrrole rings. Both the rings are forced out of plane resulting in a loss of conjugation and a reduced conductivity [118]. At first site, difference between a 3-substiuted polypyrrole and a *N*-substituted polypyrrole is marginal with respect to steric hindrance, but the conductivities differ significantly, again illustrating how are the structure property relationship. Chemical oxidative polymerization has also been applied to 3-Alkylpyrroles [106,107] and 3,4-dimethoxypyrrole [119].

The introduction of sulfonicacid group and alkyl side chain afforded water-soluble self-doped polypyrroles [120], when the sodium salt of the 3-alkylsulfonic acid pyrrole is used as monomer. It also acts as an electrolyte for the electrochemical synthesis. A second long alkyl chain on the 4-position of the pyrrole ring affords a highly ordered lamellar polymer, which is also soluble in chloroform [121]. Langmuir-Blodgett techniques have been used to improve the ordering the polypyrrole films [122,123].

Structural defects like α-β coupling are inherent to the oxidative polymerization approach and are always present in the materials synthesized according to the methods described above.

This failure to produce perfectly 2,5-linked polypyrroles has been overcome by using organometallic polymerization technique. Pyrroles with ter-butoxycarbonyl (BOC) protecting group at nitrogen have been polymerized via Stille [124] coupling, yielding a soluble non-planer precursor polymer, which was deprotected by thermal treatment [125]. This polypyrrole, although of relatively low molecular weight (approximately 16 pyrrole units), exhibits a perfect α-α structure and is fully characterized.

Recently, the reductive Ullmann [126] coupling of 2,5–dibromo-N-BOC-pyrrole has been reported to yield similar polymers to those described above [127]. Using preparative hplc, it appeared to be possible to isolate the first 20 members of the N-BOC protected oligopyrroles, which were all characterized. Similarly, a self-doped analogue of polypyrrole has been prepared using *N*–butyl-3,4-pyrrolidone in the Ullmann polymerization (**Figure-23**) [128].

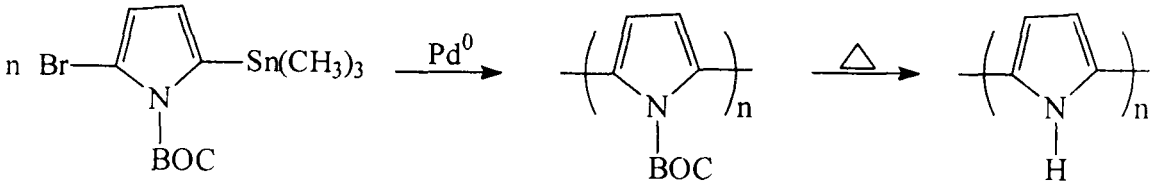


Figure-23. Polypyrrole prepared by the Stille's coupling/thermolysis sequence.

2.4. Applications of Conductive Polymers

The commercialization exemplified by the following list of materials illustrates the effects of Heeger's, MacDiarmid's and Shirakawa's work on the later development of conductive polymers. The principal interest in the use of polymers lies in low-cost manufacturing using solution processing of film-forming polymers. Light display and integrated circuits, for example, could theoretically be manufactured using simple inkjet printer technique [129,130].

Doped polyaniline is used as a conductor and for electromagnetic shielding of electronic circuits. Polyaniline is also manufactured as a corrosion inhibitor. Poly(ethylenedioxythiophene) (PEDOT) doped with polystyreneslfonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and also serve as a hole injecting electrode material in polymer light-emitting devices.

Polyphenylenevinylidene derivatives have been major candidates for the active layer in pilot production of electroluminescent displays (mobile telephone displays). Polydialkylfluorene derivatives are used as the emissive layer in full-color video matrix displays. Polythiophene derivatives are promising for field-effect transistors: they may possibly find use in supermarket checkouts. Polypyrrole has been tested as microwave-absorbing "stealth" (radar-invisible) screen coating and also as the active thin layer of various sensing devices. Other possible applications of conductive polymers include supercapacitors and electrolytic-type capacitors. Some conductive polymers, such as polyaniline show a

whole range of colors as a result of their many protonation and oxidation forms. Their electrochromic properties can be used to produce, e.g. "smart windows" that absorb sunlight in summer, an advantage over liquid crystals is that polymers can be fabricated in large sheets and unlimited visual angles. They do not generally respond as fast as in electron-gun displays, because the dopant needs time to migrate into or out from the polymer but still fast enough for many applications.

2.4.1. Polymeric batteries

One of the applications of conducting polymers, that was the focus of attention worldwide, was that of lightweight batteries. While a number of the conjugated polymers were tried, most of them failed to exhibit the desired properties, specifically with respect to stability. However, batteries made using either polypyrrole or polyaniline as the positive electrode (cathode) and lithium-aluminium alloy as the negative electrode (anode) exhibit much more respectable properties. The electrolytes in these cases were either $LiClO_4$ or $LiBF_4$ in propylene carbonate (a highly aprotic solvent, which is also fairly resistant to oxidation). During the battery discharge, electrons moves from the lithium alloy (which gets oxidized) to the polyaniline cathode (which gets reduced), as Li^+ from the anode and BF_4^- from the cathode enter the electrolyte.

One major drawback of this battery is that the energy density or energy storage capacity is low and its recyclability (charging-discharging cycles) is relatively poor. More recently, however, some composites of an alkali metal alloy and polyphenylene have been

very effectively used as anode materials in batteries that exhibit much higher energy densities, of around 65mWH/g (compared to nickel-cadmium batteries which have about 39mWH/g). In these cases, the conducting polymer serves as a binder for the alkali metal alloy, forming a multiply connected, electronically as well as ionically, conductive network within which the alloy particles are held. The mixed ionic and electronic conductivity of the conducting polymer binder allows the alloy particles to continue the electronic and ionic processes associated with the charge-discharge cycles, consequently extending the battery cycle life. Thus, the prospects of polymeric battery are still alive and are awaiting further technological refinement [131].

2.4.2. Electrochromic displays

Electrochromic display is another interesting application, which utilizes the electrochemical doping and undoping of conducting polymers. The basic idea, in such devices, is to effect a significant change in the color (both the wave length of absorption and its intensity) upon application of an electric potential. Depending upon the conducting polymer chosen, either the doped or undoped state can be essentially colorless or intensely colored. In general, the absorption of doped state is dramatically red-shifted (move to longer wave length) from that of the undoped state. Because of their very high absorption coefficients (ca. 10^5 cm^1) in the visible range of the electromagnetic spectrum, only very thin films are required to provide display devices with high contrast and a very broad viewing angle. Polyaniline, polypyrrole polythiophene and their derivatives have been successfully used to prepare prototypes of such display

devices. However, one important aspect, the cycle life, for successful commercial utilization of these materials in display devices must be considered which should be $>10^7$. A maximum of about 10^6cycles has been achieved using 50 nm thick polyaniline films, wherein the switching occurs between transparent yellow and green in less than 100ms. Thus, while these materials are yet to achieve the set target (in terms of their life cycle) for use as electrochromic displays, other interesting and innovative applications, such as electrochromic windows, for instance, are windows in buildings/automobiles which can be made to go from low transmitting (during the day) to high transmitting (during the night); the switching in such systems occurs upon application of an electric potential [132].

2.4.3. Light emitting diodes

Other exciting phenomena, that have caught the imagination of both scientists and technologists alike, are the phenomena of photo-luminescence and electroluminescence in conjugated polymers. Emission of light upon irradiation is termed as photoluminescence, while the emission on application of voltage is termed electro-luminescence. Light emitting diode is an example of utilization of the latter phenomenon. It was recently demonstrated that PPV films could be used as the emissive layer in electroluminescent devices. Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e. after thermal elimination of the precursor). Electrode materials are chosen with a low work function for use as negative, electron-injecting contact, and with a high work

function as the positive hole injecting contact. At least one of these layers must be semitransparent for light emission normal to the plane of the device. Both indium-tin oxide and thin aluminium films (7-15 nm) have been used as the transparent electrode. For polymer films, of about 100 nm, the forward voltages were as low as 10 V [133].

Further improvements, using soluble PPV derivatives such as 2,5-dialkoxy PPVs and lower work function metals, particularly calcium, as the electron-injecting contact layer, have resulted in a further drop in forward voltage to about 5 V and an increase in the efficiency to about 1% (photons per electron injected). These devices are believed to operate by double charge injection of electrons and holes from the negative and positive electrodes, respectively. These singly charged excitations combine to form excitons, which can then decay by photoemission. Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap [133].

Enhancement of the photoemission efficiency and further lowering of forward operating voltage are two of the primary areas of current activity that is expected to lead to improved devices of greater technological relevance [133].

2.4.4. Biosensors

Conducting polymers have also touched the arena of biomedical applications. One such application is the fabrication of a glucose biosensor. Such a device cannot only sense the presence of glucose but can also estimate its concentration. The principle involves immobilization of an enzyme and a suitable mediator on a conducting polymer matrix that is coated on to a suitable sensor chip. Polypyrrole and polyaniline based sensors have been fabricated, both of which are of the amperometric type (based on the measurement of the steady state current at a fixed applied potential). One such sensor is based upon electrochemically-polymerized polypyrrole on an electrode from a solution, which contains both glucose oxidase (a flavin containing enzyme that oxidizes glucose) and ferrocene monocarboxylic acid (which is the electron transfer mediator that shuttles electrons from the redox center of the enzyme to the surface of the sensing electrode).

In such a device, the amount of charge transferred (i.e., the current passed) is proportional to the concentration of glucose present in the solution. The specificity of the enzyme (which oxidizes only glucose) imparts to the device a very important characteristic, namely its ability to sense glucose even in the presence of several other components (as would be the case in, say, blood or urine). Several companies have, in fact, developed prototypes of such microamperometric glucose and galactose biosensors based on a silicon chip employing polypyrrole. These types of sensors are likely to find their way soon into analytical clinical laboratories for glucose estimation, for on-line supervision of diabetic patients etc [133].

2.5. Non Conducting Polymers

2.5.1. Polyethyleneterephthalate (PET)

Polyesters may be defined as heterochain macromolecules containing repeating ester group (—COO—) in the backbone. Natural polyester were first observed over 160 years ago and first applied in the form of synthetic glyceryl phthalate used as impregnating materials and coating during World War-I. The chemistry of polyesters developed much later as a result of extended studies by Kienle and Carothers when the fundamental theory of polycondensation process was established. They are prepared by polycondensation reaction between a dicarboxylic acid and a diol (**Figure-24**) [134].

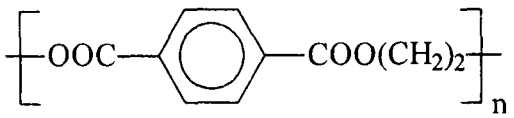


Figure-24. Chemical structure of polyethyleneterephthalate (PET).

The fiber and film forming ability of poly(ethyleneterephthalate) (**Figure-24**) was revealed by Whinfield and Dickson and today this polymer is one of the most important industrial thermoplastic polyester [134]. The starting materials for PET are ethylene glycol and terephthalic acid. Commercially dimethylterephthalate is taken in place of terephthalic acid. PET melts at around 265°C and is resistance to heat and moisture. This polymer is virtually attacked by many chemicals. It is extensively used to make textile fibers. It retains good mechanical properties up to 175°C. Tensile strength of PET film is about 25000 psi, two to three times that of cellophane or cellulose acetate film. Because of its toughness, it is applied to many typical applications such as

magnetic recording tapes. The major new application of PET for the last few years has been in the development of blow bottles [135,136].

2.5.2. Polyacrylonitrile (PAN)

Acrylonitrile, (CH_2=CHCN) was first synthesized in 1893 by Mouren [137], who was also the first (one year later) to report on an acrylonitrile polymer i.e. polyacrylonitrile (PAN) (**Figure-25**). The first synthesis of acrylonitrile was based on the dehydration of 1-cyanoethanol (ethylene cyanohydrin or acrylamide). Early industrial process for acrylonitrile production also used ethylene cyanohydrin as starting material, but since 1960 practically the entire acrylonitrile production has been based on catalytic ammonoxidation of propylene [138].

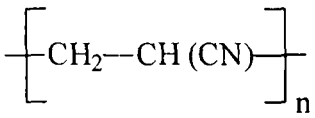


Figure-25. Chemical structure of polyacrylonitrile (PAN).

Polymerization usually carried out in aqueous solution in the presence of redox initiators. The polymer precipitates from the system as fine powder PAN softens only slightly below its decomposition temperature, PAN is soluble in DMF, THF, DMSO, acetone etc. It has heat resistance up to 220°C and exhibits good mechanical properties. It is available as films, sheets and rods [139, 140].

2.5.3. Cellulose acetate (CA)

Cellulose is the main constituent of the cell walls of plants. Usually two sources of cellulose are utilized for the preparation of the

cellulosic plastics; they are cotton and wood pulp. Cellulose is a naturally occurring, linear, stereo-regular polysaccharide made up of α-D (+)-glucose units, joined by 1,4-glucoside linkages. High intermolecular forces and regular structure of the polymer result in its having an unusually high degree of crystallinity. It has very high melting point and in fact it decomposes only before beginning to melt [141,142].

Cellulose acetate is prepared by reacting natural cellulose (like cotton, wood) with acetic anhydride or glacial acetic acid in presence of a catalyst (such as sulfuric acid or perchloric acid). The resultant cellulose acetate ether is partially hydrolyzed so that about 2 to 2.5 acetate group per $C_6H_{10}O_5$ unit remains and the product become soluble in organic solvent like acetone. The triacetate of cellulose is less soluble in common non-toxic solvents. Hence, the more soluble secondary acetates are commonly used.

$$\underset{\text{(Cellulose)}}{-[C_6H_7O_2(OH)_3]_n-} + 3nCH_3COOH \xrightarrow{H_2SO_4} \underset{\text{(Cellulose triacetate)}}{-[C_6H_7O_2(OCOCH_3)_3]_n-} + 3nH_2O$$

$$\underset{\text{(Cellulose triacetate)}}{-[C_6H_7O_2(OCOCH)_3]_n-} + nH_2O \xrightarrow{\text{Hydrolysis}} \underset{\text{(Cellulose diacetate)}}{-[C_6H_7O_2(OH)(OCOCH_3)_3]_n-} + nCH_3COOH \qquad (13)$$

Cellulose acetate is colorless, odorless, tasteless, tough and durable plastic with a density ranging from 1.2-1.4 g/cc. It has good impact strength and can easily be machined and molded. It burns very slowly and is resistant to most household chemicals, oils, gasoline and cleaning fluids. It is prone to attacks by acids, alkalis and acetone. It has good electrical insulating properties and low shrinkage. It is used in the

form of films, sheets, rods, tubes and sections. It is also used in the manufacture of radio appliances, automobile steering wheels, handles, windows, goggles, combs, musical instruments, photographic and X-ray films etc. [143,144].

2.5.4. Polyamides

The chemistry of synthetic polyamides started in 1862 when Harbordt [142] obtained an insoluble and infusible powder by reacting hydrogen chloride gas with *m*-aminobenzoic acid at 200°C, which we called poly(3-benzoamide). The first aliphatic polyamide reported by Gabril and Maas in 1899 [145] is polyhexaneamide. With the clear object to obtaining high-molecular weight polyamide,

Polyamides are condensation products having amide groups (-CONH-) as integral part of the main polymer chain. There are number of polyamides found in nature such as casein, wool, silk, various proteins etc. Synthetic polyamides are produced by condensation reaction between monomers in which the linkage of the molecules occurs through the formation of the amide groups. They may be produced by the interaction of a diamine (a compound containing two amino, $-NH_2$ groups) and a dicarboxylic acid such as lactum. They may also be formed by self-condensation of an amino acid or an amino derivative. The most important amide polymers are nylons and aramides an extremely versatile class of material that is an indispensable fiber and plastic [146].

The birth of nylon was an epoch-making event in human history. Coming to the world after aluminum, the last arrival (1886) in the metallic age. Nylon was the first fully artificial polymer material that opened the plastic age.

In October 1938, Du Pont USA announced the invention of the first wholly synthetic fiber ever produced. The scientists of the ICI GROUP of London found similar results. Hence, to give recognition to both the groups, the product obtained by condensation polymerization of hexamethylenediamine and adipic acid was named NYLON, NY for New York and LON for London. But generally Carothers and his associates are credited with the synthesis of the first nylon. The material was actually polyhexamethylene-adipamide, also known as nylon-6,6 for the presence of six carbon atoms in each of its two monomers. Soon after the Du Pont, fiber produced in Europe was marketed as nylon-6 (polycaprolactam) [145].

Nylons are aliphatic polyamides. They are linear structure and are thermoplastic in nature. The polymer chains have polar -CONH- groups spaced out by methylene links of various lengths, depending upon the type of nylon. The presence of polar groups in nylons creates greater inter-chain interaction, which leads to higher melting point for polymers. Nylons are good insulators at high as well as low frequencies. However, they cannot be used as insulators under humid conditions, as they absorb water. So Nylon-6 (**Figure-26**) and nylon-6,6 (**Figure-27**) have almost the same structure and similar properties.

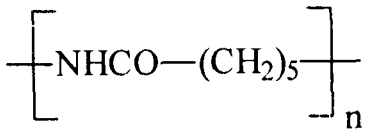


Figure-26. Chemical structure of nylon-6.

Nylon-6 has melting point of 250°C. It has good tensile strength, abrasion resistance and toughness up to 150°C. It is generally unaffected by dry-cleaning fluids. It has excellent stability against alkalies. light degrades this polymer just like any other textile fiber. It is resistant to weak acids, alkalis (weak and strong), esters and hydrocarbons. Strong acids attack it, however, formic acid and phenols dissolve this polymer. Nylon-6 is used in the manufacture of gears, bushes, dry pumps, cams, slide fasteners, door hinges, gaskets, tire cords, bristles etc [146,147].

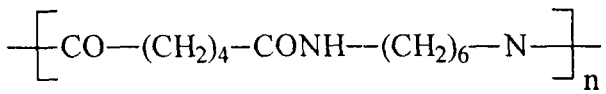


Figure-27. Chemical structure of nyion-6,6.

Nylon-6,6 has melting point of 250°C. It also has good tensile strength, abrasion resistance and toughness up to 150°C. It is generally unaffected by dry-cleaning fluids. It has excellent stability against alkalis. It is resistant to many solvents, however, formic acid, cresols and phenols dissolve this polymer.

Nylon-6,6 is also used for making gears, cams, dry bearings, and dry pumps, guide bushes etc. It is used to make tire cords, ropes and monofilaments. Moldings made of sterilized grade nylone-6,6 are used

in pharmacy and medicine. It has been used for packaging foodstuffs, hydrogenated vegetable oils, gee etc. It is also used to prepare bristles, wigs, sports equipment etc. Fiberglass reinforced nylon-6,6 is used in manufacturing of car components, in different military and electrical applications [146,148].

2.6. Polyaniline Composites

Sifullina et al. [149] reported the electrochemical synthesis of polyaniline composites in porous polyethyleneterepthalate (PET) and polyethylene (PE) matrices prepared by solvent crazing. Electrochemical polymerization of aniline in porous matrices produced highly dispersed polyaniline, of morphology different from that of polyaniline prepared in absence of matrices. Distribution of polyaniline in the porous matrices was observed to be dependent on the mode of solvent crazing and the extent of drawing of the solvent crazed polymer.

Kalhon et al. [150] reported the surface grafting of polyaniline on silica by chemical polymerization. Whereas the change in electrical conductivity of composite of polyaniline and poly(ethylene-co-vinyl acetate) was investigated by Tsanov et al. [151]. It was observed that the fraction of polyaniline at which conductivity jump occurs, is not constant during aging as well as during storage. The electrical conductivity of the films of low polyaniline, content (up to 2.5 wt %) increased by several orders of magnitude over a period of eight months storage. It was proposed that the polyaniline, phase undergoes flocculation, which subsequently forms a continuous conductive network. The electrical conductivity jump was attributed to the dynamic interfacial interactions between the constituents of the composites.

Conductive blends prepared from plasticized cellulose acetate and polyaniline protonated with sulfonic acid, phosphonic acid and phosphoric acid were observed to be highly transparent. Films casted from *m*-cresol solution showed a percolation threshold below 0.5 wt.% and excellent mechanical properties [152].

A green colored porous vycor glass composite with polyaniline was prepared by oxidative polymerization of aniline on aniline impregnated porous vycor glass. Exposure of composite to NH_4OH solution leads to a reversible color change from dark green to dark blue [153]. Jan et al. [154] prepared composites of polyaniline with vinylidene chloride-co-rnethylacrylate and co-butylacrylate copolymers by chemical method. Appropriate polymerization conditions made it possible to obtain composites containing 5 to 50 % of polyaniline in the composite and the electrical conductivity was observed to be 1.5 S/cm.

Charge transport studies were reported on camphor sulfonic acid doped composite of polyaniline with nylon-12 (CSA-PANI/Nylon-l2) and toluene sulfonic acid doped composite of polyaniline with carbon black (TSA-PANI/CB). The CSA-PANI/Nylon-12 showed a temperature dependent insulator-metal transition and anomalous high microwave adsorption whereas the TSA-PANI/CB showed an unusual insulator to metal transition from the individual materials to the composites. A common mechanism was suggested for the inhomogeneous charge transport due to the formation of ordered regions during the polymerization of conducting polyaniline in both the composites [155].

Electrical conductivity of polyaniline and polycarbonate composite could be increased more than 15 orders of magnitude by a small variation in amount of polyaniline in composite as explained by percolation model. The percolation threshold and critical exponent of electrical conductivity suggests the anisotropy in electrical conductivity while highly conducting composite is found to be stable up to 160°C in terms of electrical conductivity [156].

Percolation threshold of electrical conductivity of emulsion polymerized polyaniline-chlorosulfonatedpolyethylene copolymer and polyaniline-styrene-butadiene terpolymer composites were observed to be 21% and 70% respectively. However, it increased two orders of magnitude and exhibited a new percolation threshold at 3.0% for both the composites after secondary doping by *m*-cresol. The secondary doping noticeably increased permanent set change with polyaniline content as well as changed the ductile fracture into the brittle fracture. Secondary doping did not show any marked effect on tensile strength and elongation [157].

Young et al. [158] reported the preparation of electrically conductive polyaniline:polystyrene composites by *in-situ* polymerization and blending. The electrical conductivity of polyaniline:polystyrene composites was improved with increasing amount of polyaniline and reached to a high value of 0.1 Scm^{-1} at a content of 12 wt% as calculated by elemental analysis. The composites were found very soluble in organic solvents such as chloroform, xylene, N-methylpyrrolidone (NMP) while electrical conductivity of composites, doped with dodecylbenzenesulfonic acid and thermally

treated at 180°C for 3 hours showed good stability. A conductive nylon6:polyaniline composite for rechargeable battery electrode and for liquid crystal display with improved mechanical strength and electrical stability was also reported [159].

Phase separation and conductive pathways formation was observed in polyaniline:polyethylene-co-vinylacetate composite films resulting in the formation of polyaniline enriched lower side layers during storage. A distinct difference in the electrical conductivity of the two sides of the films was detected. A mathematical interpretation of the evolution in percolation behavior of polyaniline:polyethylene-co-vinylacetate composites versus time is presented. The unstable conducting properties (both the electrical conductivity jump and phase separation phenomenon) of polyaniline:polyethylene-co-vinylacetate composites over time revealed their dissipative nature supporting the dynamic interfacial model of conductive polymer composites [160]. Zheng et al. [161] used electrochemical technique to synthesize highly conducting polyaniline:polyvinylacetate composite films using perchloric acid as a dopant as well as oxidant. Electrical conductivity was observed to be 0.173 Scm^{-1}.

Synthesis and characterization of highly conducting polyaniline:clay nanocomposite with extended chain conformation was reported by Qiuju et al. [162]. The conductive emeraldine salt form of polyaniline was inserted into the galleries of montmorillonite to produce the hybrid with highly conducting polyaniline. The product obtained was a nanocomposite and over 90% of polyaniline chains were inserted

between the layers. It was also found that the polymerization is a diffusion-limited process.

A composite of polyaniline (PANI) encapsulating titanium oxide (TiO_2) particles of nanometer size has been synthesized by *in-situ* emulsion polymerization. Particle dimensions have been measured and the nature of the association between the components have been studied using SEM and TEM techniques. The interaction between PANI and TiO_2 and the nature of chain growth have been investigated and explained with the help of FTIR spectroscopic studies. The improvement in thermal stability and crystallinity of nanocomposites of polyaniline and TiO_2 has been evaluated by using TGA and XRD. The mechanism of charge transport and photo induced charge *trans*fer in composites have also been reported [163].

Polyaniline thermally blended with butadiene-styrene rubber at different weight composition and then was capillary extruded to fibers. Microscopic analysis on the extrudates revealed that polyaniline was deformed during the process to produce elongated structures i.e. ellipsoids or even short fibers in the blends. Electrical measurements were performed and it was found that blends with more than 20 weight percent polyaniline could produce an electrically conductive composite with a good level of conduction. The relationship between the volume conductivity and content of polyaniline in the blends showed the characteristics of a percolation system, with a threshold as low as 5-weight % of polyaniline [164].

Oyama et al. [165] reported a composite of 2,5-dimercapto-l,2,4-thio-diazole and polyaniline on a copper current collector that provides high charge density exceeding 225 Ah/Kg cathode with average discharge voltage at 3.4 V. The composite cathode showed excellent rate capability and cyclability of >500 cycles. While large increase in the charge density to 550 Ah/Kg cathode is achieved by adding elemental sulfur (S_8) to the composite cathode.

A conducting elastomeric foam composite from an elastomer foam and polyaniline was reported by Bessette et al. [166]. Only 5% of conductive polymer is required for insulator to conductor transition and the electrical conductivity of the composite foam could be effectively controlled between 10^{-7} and 10^{-1} Scm^{-1} by varying the amount of oxidant used and/or by variation in the copolymer composition.

Several protonated poly(*o*-anisidine) and polyvinylalcohol composites were prepared using different types of acids such as sulfuric, *p*-toluenesulfonic, camphorsulfonic and *p*-dodecylbenzene-sulfonic acids. The linear dependence of the log of electrical conductivity on the variation of humidity was observed for all the composites, which was caused by the salt-base transition of the conducting polymer composite i.e. by the movement of free acid between the active sites of the conducting polymer and the strongly bound water existing in polyvinylalcohol, which in turn depends directly on the environmental humidity. The response time of the composites to humidity was shortened with a decrease in the size of the dopant anions [167]. The composite of polyaniline and its

derivatives with polyvinylalcohol were observed to be useful materials as humidity sensors by Shiigi et al [168] also. Certain composites like poly(*o*-phenylenediamine) and poly(*o*-aminophenol) with polyvinylalcohol exhibited linear dependence of electrical conductivity versus atmospheric humidity whereas those of poiy(m-phenylene-diamine) and poly(*o*-toluidine) with polyvinylalcohol showed non-linear dependence on humidity without hysteresis. H. Shiigi et al. [169,170] prepared composites of polyaniline and its derivatives with polyvinylalcohol. They developed sensors based on this composite to detect carbon dioxide and humidity.

A conducting composite of polyaniline and polycarbonate was prepared by blending using chloroform as a solvent by Lee et al. [171]. Polycarbonate containing sulfo group enhance the Coulombic interaction between two phases of the composite. The effect of ionic groups in sulfonated polycarbonate was monitored using measurements of both the mechanical and thermal properties. The electrical conductivity was increased to 7.5 Scm^{-1} on doping with camphorsulfonic acid or dodecylbenznesulfonic acid.

Iroh and Rajagopalan [172] electrochemically codeposited polyaniline and polypyrrole on carbon fibers under potentiostatic conditions. Electropolymerization was carried out by varying the applied potential and the feed ratio of monomers. Weight gain plots indicated that polyaniline is preferentially formed when the monomer ratio is 90% aniline; 10% pyrrole, however, more polypyrrole was formed as pyrrole concentration increased. The thermal stability of the composites was observed to be between the stability of homo-polymers of the

components. The morphology of the composite was affected by the polymerization potential and monomer feed ratio.

An improvement in the electrical conductivity of polyaniline:nylon-6 composite fabrics was observed on surface modification of nylon-6 fabrics by various plasma treatments by Oh et al. [173]. Electrical conductivities of polyaniline:nylon-6 composite fabrics were highly increased by ultrasonic treatment, which assisted the diffusion of aniline in to the inside of nylon fabrics by cavitations and vibration. The fabric conductivity was also observed to increase with increase in monomer concentration and the polyaniline deposition cycles. Park et al. [174] prepared polyaniline:polyacrylonitrile composite by electrochemical polymerizing aniline on the polyacrylonitrile coated platinum electrode and they compared the properties of the composite with that of the polyaniline.

2.7. Electrochemistry of the Cell

The invention relates to a conducting organic polymer battery, and more particularly a battery containing a conducting organic polymer doped with a polymer anion as a cathode and a metal as an anode, wherein anion concentration of an electrolyte solution therein does not substantially change during charging and discharging.

It is known that a combination of a p-type conducting organic polymer as a cathode and a metal having a lower redox potential than that of the polymer as an anode can provide a secondary battery capable of charging and discharging as described [175-177].

p-type conducting organic polymers which have conventionally been used in the above-described secondary batteries are polymers that are cationic by themselves and are doped with a low molecular weight anion, such as perchlorate, chloride and tetrafluoroborate ions. On reduction in an electrolyte solution, they become neutral by releasing the dopant anion and, on reoxidation. They capture the anion again. In other words, p-type conducting organic polymers having a low molecular weight anion as a dopant and have a reversible anion incorporating ability.

On the other hand, the metal used as an anode becomes a metal ion upon oxidation in an electrolyte solution and dissolved in the electrolyte solution. On reduction, the metal ion is deposited on the anode.

In a conventional battery, cathode comprises of the above-described conducting organic polymer, which is cationic and is doped with a low molecular weight anion and anode comprises of a metal. During discharging, anion X^- is released from the cathode and cation M^+ is released from the anode, whereby the ion concentration in the electrolyte solution increases considerably. On the other hand, these reactions are reversed during charging. That is, anion X^- is incorporated into cathode and metal ion M^+ is precipitated on the anode, whereby the ion concentration in the electrolyte solution markedly decreases. It is, therefore, apparent that the charging and discharging characteristic of batteries of this type depend on diffusion into and out of polymer electrode.

In these conventional batteries, it is necessary to use an excess of unsaturated electrolyte solution relative to the volume of the conducting organic polymer and the metal from considerations that the ions released from both cathode and anode on discharging should be dissolved in the electrolyte solution and that the internal resistance of the battery should be reduced by maintaining a sufficient ion concentration of the electrolyte solution during charging. Therefore, such batteries have a relatively high energy density as calculated from only the weight of the electrode active materials, they have a seriously poor energy density when taking into consideration the weight of the electrolyte solution also, which has been a serious problem to their practical application.

The inventors previously proposed p-type conducting organic polymers doped with a high molecular weight polymer having a number of anionic group in the molecule thereof in place of the above-described low molecular weight anion, as reported in Ohtani et al. [178]. In marked contrast to the p-type conducting organic polymer doped with a low molecular weight anion, since the polymer anion as a dopant is hardly diffusible in the conducting organic polymer because of its high molecular weight, the conducting organic polymer incorporates a cation in the electrolyte solution within its molecule by reduction of the conducting organic polymer in the electrolyte solution and then releases the cation thus incorporated upon re-oxidation of the conducting organic polymer. That is, the p-type conducting organic polymer doped with the polymer anion possesses a reversible cation-incorporating ability. There has also been proposed a plastic battery containing the above-described conducting organic polymer doped with a low molecular weight anion

as a cathode and a conducting organic polymer doped with the above-described polymer anion as an anode as disclosed in a Japanese Patent [179].

Conducting organic polymers are obtained by electrolytic oxidative polymerization, chemical oxidative polymerization or photo-oxidative polymerization of heterocyclic compounds, e.g. pyrrol, thiophene and their derivatives and aromatic compounds, e.g. aniline, phenol, polyacetylene and their derivatives and so on.

Examples of the polymer anion to be used as a dopant include polyvinylsulfonic acid, polyvinyl sulfuric acid, polystyrensulfonic acid, a sulfonated styrene butadiene copolymer, polyallylsulfonic acid, polymethallyl sulfonic acid, poly-2-acrilamide-2-methylpropane-sulfonic acid, a halogenated acrylic acid polymer, etc. In addition, fluorine-containing polymers commercially available under a trade name of "Nafion" are also useful as a polymer anion. These polymers have a number of sulfonic acid groups on the molecular side chain thereof. In the present invention, the polymer anion is not limited to above materials.

The metal which can be used as an anode is a metal having a lower redox potential than that of the above-described conducting organic polymer. Lithium, zinc and magnesium are preferably used. The battery wherein electricity passes from the cathode towards the anode can be obtained, the battery namely charged, by applying a proper voltage between the two electrodes via a potential loading device to cause a reverse electrode reaction.

The solvent for the electrolyte solution as an ion-conductive phase usually includes organic solvent, e.g. propylene carbonate, dimethoxyethane acetonitrile, dimethoxymethane, sulforane, dimethylesulfoxide, dimethoxylformamide, γ-butyrolactone, benzonitrile, N-methyl-2-pyrrolidone, dimethylacetamide, water and mixed solvents of water and the above-enumerated organic solvents. In particular, the solvent to be used is preferably selected from those which exhibit low reactivity with the cathode comprising of conducting organic polymer and the metal anode, do not participate in the redox reaction during charging and discharging and are not liable to deterioration.

The electrolyte is not particularly limited, examples thereof include lithium tetrafluoroborate, lithium perchlorate, lithium hexafluorophosphae, lithium hexafluoroarsenate, zinc sulphate, zinc chloride, magnesium chloride, magnesium sulphate etc. Appropriately selected from those containing the same metal component and used in the metal anode and whose anion component in the electrolyte does not participate in the redox reaction during charging and discharging.

At the same time, a reverse voltage is applied between the electrodes to oxidize the p-type conducting organic polymer having a cation-incorporating ability and, to reduce the metal ion for discharging. As a result, the conducting organic polymer releases the cation M^+ is precipitated as a metal on the anode thereby regenerated by the battery. Accordingly, the ionic concentration in the electrolyte solution does not change substantially during charging as well as discharging.

2.8. Diffusion in Polymers

2.8.1. Fick's law

Generally diffusion occurs by local activated jump of a diffusant to neighboring unoccupied hole in the polymer matrix. Similarly in most molecular solids diffusion occurs via point defect, i.e; empty sites in the lattice. In both the cases, it can be reperesented by Fick's law of diffusion.

$$J_D = -D\left(\frac{dc}{dx}\right) \tag{14}$$

where J_D is the diffusive flux (number of diffusant particles crossing a plane perpendicular to the direction of motion, per unit area per unit time) and c is the concentration of the diffusant in a distance, x, after time t. D is the effective diffusion coefficient of the diffusing species in the solid. From this, we can deduce the second law of diffusion, which can be written for one-dimensional system as

$$\left(\frac{dc}{dt}\right) = D\left[\frac{d^2c}{dx^2}\right] \tag{15}$$

and for three dimensional systems as:

$$\left(\frac{dc}{dt}\right) = D\left[\left(\frac{d^2c}{dx^2}\right) + \left(\frac{d^2c}{dy^2}\right) + \left(\frac{d^2c}{dz^2}\right)\right] \tag{16}$$

The mathematical solutions for these differential equations for different boundary conditions have been given by Crank [180]. Materials, which obey these mathematical equations for their

diffusional behaviors, are said to *follow* Fickian diffusion [181].

2.8.2. Factors affecting diffusion

Different factors affecting diffusion are temperature, polymer morphology, the diffusant size and concentration, diffusant solubility in the polymer, electrostatic interactions and impurities [181].

2.8.3. Effect of temperature

In a real three dimensional isotropic systems, the expression for the diffusion coefficient is given by the equation:

$$D = g\nu n a^2 \exp^{(-H/KT)} \qquad (17)$$

where ν is the frequency of vibration of the diffusing species, a is the jump distance (Le. average distance between two neighboring holes), n is the number of defects or hores, g is the geometric factor, H is the potential barrier to be surmounted by the diffusant, k is the Boltzmann constant and T is the temperature. If g, ν, n and a are constants, the equation is the modified form of the Arrhenius equation expressing the relation between diffusion coefficient and temperature [182]. The diffusion coefficient very often follows an Arrhenius type of relation similar to that given in equation (above). Thus, it must be made clear that with an increase of temperature, H, a and ν will change slightly, affecting the diffusion coefficient. These changes are smaller compared to the expotential change in d but can causes a slight curvature in the plot [181].

2.8.4. Effect of polymer morphology

Ionic motion in a conducting polymer is influenced by any factor affecting the number, size and distribution of pre-existing holes and. the ease of hole formation. The potential energy barrier for the diffusant is expected to be low if the neighboring polymer segments can very easily rearranges themselves to let the diffusant molecules pass through. Hence, it can be assumed that the factors causing obstruction segmenta (mobility would decreases the transport of diffusant in the polymer and would increase the activation energy [181,183,184].

2.8.5. Effect of the diffusant size and concentration

Generally, diffusants smaller than the size of the monomer unit of the polymer, diffuse faster than organic liquids or vapors and their activation energy and coefficient of diffusion are independent of concentration of the diffusant present in the polymer [185, 186]. In this case, the size of the diffusant molecule is smaller than the average hole size in the polymer matrix and diffusion takes place by simple activated jumps from *one* hole to another unoccupied hole. On the other hand, the diffusion of larger diffusant molecule is often concentration dependent, requiring much greater number of polymer segments to rearrange by micro-Brownian motion as the hole of appropriate size are few in number [183,184,187]. Thus with increasing diffusant size, diffusion coefficient decreases with increasing activation energy, which can consistently be explained by the hole concept. In case of a typical insulating polymer matrix, the decrease in activation energy results in the increase of the diffusion coefficient with increase in the diffusant concentration [181].

2.8.6. Effect of diffusant solubility in the polymer

The solubility of diffusant in the host material, may have definite effect on diffusion properties. Thus the rate of diffusion is showed down by the factors enhancing solubility and opposite is true for many diffusant systems and for semi-conductors [180,181,188].

2.8.7. Effect of electrostatic interactions

The doped states of the conducting polymers is assumed to be as a solid electrolytic solution in which the conducting polymer chains carry positive charge and dopant ions carry negative charges (p-type doped) or vice-versa (n-type doped). The increase in the dopant ion concentration must intensify the ion-ion, chain-chain and chain-ion electrical interactions. The charge density on the dopant ion must diminish as the size increases. The better stabilization of the dopant ions in the charged polymer matrix and the severe repulsive force between the charged dopant ions preventing their free movement, may lead to higher activation energy and lower coefficient of diffusion [181].

However, repulsive electrostatic interaction between charged polymer chains would try to keep the chains apart from each other may lead to a rower activation energy and higher coefficient of diffusion [181].

2.8.8. Effect of impurities

The presence of impurities can influence diffusional properties to a great extent in a number of ways. In semi-conductors impurities produce local distortions in the crystal lattice, but however, with ionic

impurities, electrostatic interactions have to be considered. In general, uniformly distributed donor impurities tend to reduce the diffusion rate of acceptors and increase that of donors whereas reverse is true for donor impurities [181,188].

2.9. Objectives

As evident from the literature cited in the preceeding sectors, the electroactoive polymers have emerged as potential materials due to their excellent electrochemical properties. Their composites with non-conducting polymer matrices are also very promising materials for use in charge storage devices. These Composites possess outstanding chemical and mechanical properties. Keeping in view the above facts, the experiments were designed with the following specific objectives.

1. Preparation and characterization of electrically conducting composites based on polyaniline and nylon-6,6.

2. Study of electrical properties of composite films.

3. Study of stability of composites under isothermal conditions in term of DC electrical conductivity retention.

4. Study of charging/discharging behavior of composite films.

5. Study of diffusion coefficient.

Chapter-Three
Experimental

CHAPTER-3

3. EXPERIMENTAL

3.1. Reagents and Instruments

Ammonia solution, Qualigens, India Ltd., (used as received), Acetone, 99%, Qualigens, India Ltd. (used as received), Formic acid, 88%, CDH, India Ltd., (used as received), Hydrochloric acid, 35%, E.Merk, India Ltd., (used as received), Nylon-6,6, Dupont, Ltd., Potassium persulphate, 98%, CDH, India Ltd. (used as received), Electrically operated automatic pressure machine (TSI) Model PF-A15, Dry box, 9V Battery, On-off key and Digital micro-voltmeter, Model DMV-001 (Roorkee India).

3.2. Preparation of Polyaniline:nylon-6,6 Composite Films

Nylon-6,6 pieces were cut into square shaped, such that each sample weighed (0.2658 g) and then these pieces were pressed into thin films by an Electrically Operated Automatic Pressure Machine at different pressure (in tons). We obtained films of different thickness viz. 0.4, 0.5 and 0.6 mm with respect to 10, 8, and 6 tons pressure at constant temperature of 220°C.

Nylon-6,6 films were kept separately in 30 ml doubly distilled aniline for different periods of time in an air oven at 80°C to allow aniline diffuse into nylon-6,6 matrix. During this process, some nylon-6,6 was also dissolved in the aniline as nylon-6,6 in the aniline was converted into gel above 80°C. Aniline soaked films were treated with

0.1M potassium persulphate in 1M HCl solution and left for 24 hours at ice temperature in order to polymerize aniline within the nylon-6,6 matrix. After polymerization, Polyaniline:nylon-6,6 composite films were obtained. These films were washed with doubly distilled water up to acid neutralization. After that films were undoped by treatment with excess of 25% aqueous ammonia and repeatedly washed with distilled water until the filtrate became neutral. The composite films were dried for 24 hours at 40°C in a dry box and then stored in desiccators for experiments.

3.3. Doping of Composite Films

Polyaniline:nylon-6,6 composite films were doped by treating with 1M HCl solution. The Composite films were treated with 200 ml of 1M HCl solution in a glass beaker and left at room temperature for 24 hours.

3.4. Characterization

3.4.1. FTIR spectroscopic studies

FTIR spectra of polyaniline:nylon-6,6 composites were recorded by Nicolette-Protégé 460.

3.4.2. Scanning electron microscopic (SEM) studies

For the study of the difference in surface morphology between the parent materials and their composites, SEMs were performed by LEO-435 VP SEM instrument.

3.4.3. DC electrical conductivity measurements

DC electrical conductivity of the doped composites films were measured with increasing temperature by using a four-in-line probe DC electrical conductivity-measuring instrument. DC electrical conductivity (σ) was calculated using following equations:

$$\rho = \frac{\rho_0}{G_7(W/S)} \tag{18}$$

$$G_7(W/S) = \left(\frac{2S}{W}\right)\ln 2 \tag{19}$$

$$\rho_0 = \left(\frac{V}{I}\right) 2\pi S \tag{20}$$

$$\sigma = 1/\rho \tag{21}$$

where σ, ρ, ρ_0, I, V, W and S are DC electrical conductivity (S/cm), corrected resistivity (ohm cm), uncorrected resistivity (ohm cm), current (A), voltage (V), thickness of the film (cm) and probe spacing (cm) respectively [1]. G_7(W/S) is a correction divisor, which is a function of thickness of the sample as well as probe spacing. The sample to be tested is placed on the base plate of four–probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure is applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply is then switched on, the temperature was allowed to increase gradually the current and voltage were recorded simultaneously with rise in temperature.

3.4.4. Isothermal technique

The thermal stability of composite samples in term of DC electrical conductivity retention was studied under isothermal conditions by using four-in-line DC electrical conductivity measuring instrument. This study was carried out at 50°C, 70°C, 90°C, 110°C and 130°C on the selected composite films. The electrical conductivity measurements were done at an interval of 10 min. The data obtained for samples were plotted as log σ versus1000/T(K).

3.5. Preparation of Cathode Active Materials

The preparation of polyaniline:nylon-6,6 composite films (as a cathodic material) was done by immersing aniline monomer(doubly distilled) in nylon-6,6 films. The immersed films of different thickness viz. 0.40, 0.50, 0.60 mm treated with 0.1M potassium persulphate in 1M HCl for 24 hours in order to polymerize aniline within the nylon-6,6 matrix. The films were taken out and washed with doubly distilled water, undoped by treatment with excess of aqueous ammonia (25%) and repeatedly washed with distilled water until the filtrate became neutral. The composite films were redoped with 1M HCl for 24 hours and then dried for 48 hours at 45°C in a dry box and then stored in desiccators for experiments.

3.6. Set up of Electrochemical Cell

The positive electrode consisted of a PANI:Ny-6,6 composite film, Al/Zn foil as a negative electrode and Pt foil used as a reference electrode to monitor the potential of PANI:Ny-6,6 cathode during experiment. An equal area of each electrode was immersed in 40 ml of aqueous/non-aqueous solution in a glass beaker. Polyaniline is electroactive only in acidic media [2]. The positive pole of 9-volt

battery was connected to counter electrode (Zn/Al) foil by Teflon coated platinum wire and the negative pole of the battery was connected to the working electrode (PANI:Ny-6,6 composite film). On the other hand the reference electrode was connected to the digital micro-voltmeter as shown in **Figure-28.**

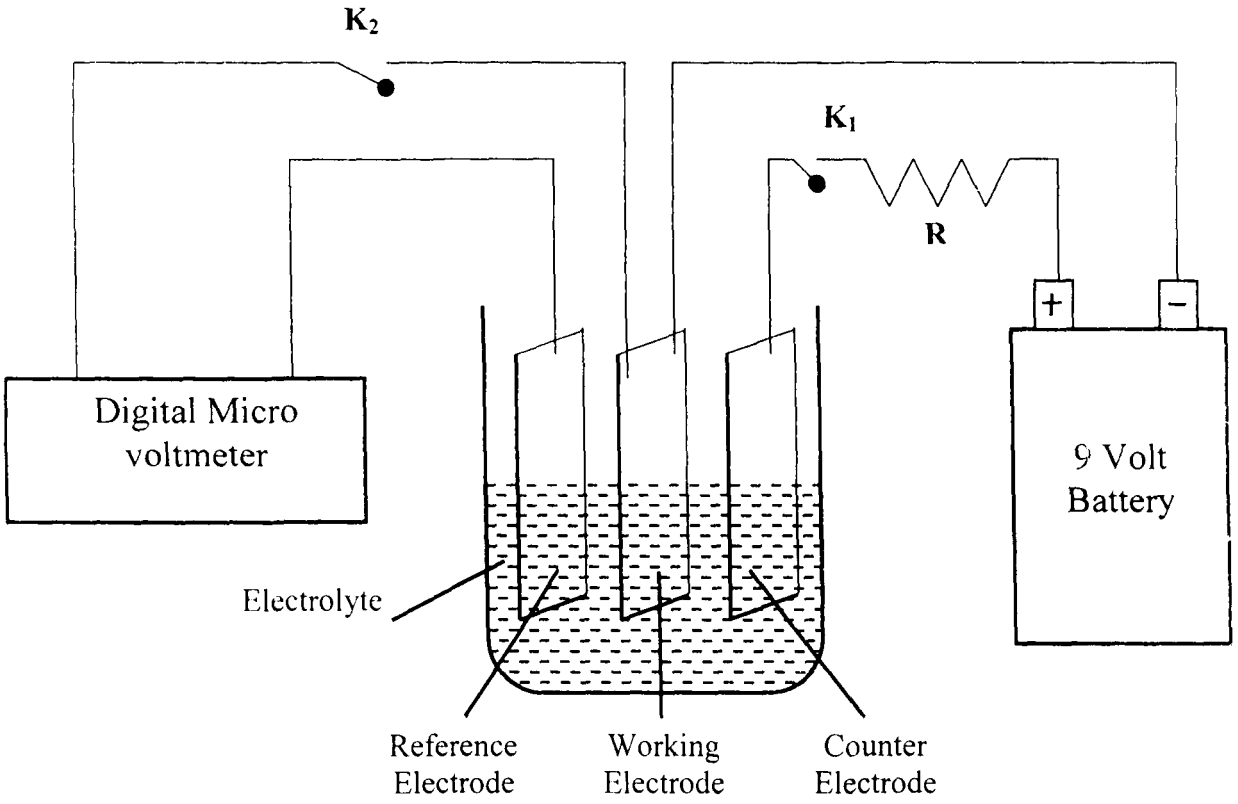


Figure-28. Set up of electrochemical cell.

3.7. Estimation of Dopant Ion Concentration

It is essential to know that the extent of dopant present in the polymer for the estimation of the diffusion coefficient, therefore, as-prepared polyaniline:nylon-6,6 composite films were undoped in electrochemical cell containing appropriate electrolyte solution by applying a limiting current of few-microamperes at 40°C, some before and some after diffusion measurements, to establish that there is no loss of dopant by any other reaction such as moisture compensation during data acquisition. The voltage against an aluminum electrode was recorded at regular intervals [3].

$$\text{Mol. Ratio (y)} = \frac{i\, t\, M_m}{FW} \qquad (22)$$

$$\text{Dopant concentration (C)} = \frac{y\, d}{(M_m + y\, M_d)} \quad \text{mol cm}^{-3} \qquad (23)$$

where C is the dopant concentration in polymer, y is the mol ratio (number of mol of dopant present per monomer unit), I is the strength of the current passed (A), t is the time taken in undoping (s), M_m is the formula weight of monomer residue (g), F is the Faraday's constant (96487 C mol^{-1}), w is the weight of polymer (g), d is the density of the polymer and M_d is the formula weight of dopant ion (g).

3.8. Estimation of Diffusion Coefficient

The various techniques available for ionic diffusion measurement have been discussed briefly with the merits and demerits of their use for different types of materials by Foot [4]. The galvanostatic pulse

technique has been used very successfully to estimate Li^+ ion diffusion in TiS_2 by Winn et al. [5] and in $NiPS_3$, $FePS_3$ and FePSe3 single crystals by Foot [4].

In this method a constant current pulse is passed through the equilibrated electrode material. This causes a change in the electrode potential against a standard electrode due to deposition of a quantity of ions equivalent to IP/F on the electrode surface. An amount of 10^{-10} to 10^{-8} mol. of dopant (depending upon strength of pulse) was deposited on the polymer electrode as the diffusion equation would be valid only for small changes in electrode potential i.e. small change in y value. Clean Al or Pt foil was used as standard electrode. Potential of this "quasi-standard" electrode may be assumed to be constant during the experiment, as equilibration does not take too long. As the deposited ions diffuse into the electrode material, the surface concentration changes and the electrode potential recovers. A plot of recovery voltage (E_t) against $t^{-1/2}$ should follow a straight line, if the diffusion behavior is governed by Fick's law. The following expression was used for the estimation of the diffusion coefficient for the ions into and out of the electrode material.

$$\text{Exp}\ \frac{(E_t - E_o)\ F}{R\ T}\ -1 \quad = \quad \frac{I\ P}{(1-y)\ F\ A\ C_o \sqrt{\pi}\ D\ t} \qquad (24)$$

Plot of $(E_t - E_o)$ versus $t^{-1/2}$ follows a straight line of slop,

$$S = \frac{I P R T}{(1-y)^2 F^2 A C_o \sqrt{\pi} D t} V t^{1/2} \quad (25)$$

$$D\pi = \left[\frac{I P T R}{(1-y)^2 F^2 A C_o S}\right]^2 \quad (26)$$

$$D = \frac{I^2 P^2 T^2 R^2}{(1-y)^4 F^2 A^2 C_o^2 S^2 \pi} \ cm^2 S^{-1} \quad (27)$$

where I is the current strength of impulse (A), P is the duration of the impulse (s), R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), T is the experimental temperature (K), F is Faraday's constant (96487 mol^{-1}), A is the area of working electrode (cm^2), C_o is the dopant concentration in the composite film ($molcm^{-3}$), (1-y) is the concentration correction factor and E_o is the original equilibrium potential of the electrode. This method is preferred because during data acquisition, the current does not pass through the electrode material. So no correction has to be made for electron transfer kinetics or variable Ohmic (IR) potential difference.

Chapter-Four

Results & Discussion

CHAPTER-4

4. RESULTS AND DISCUSSION

4.1. General

Electrically conductive and mechanically robust composite materials have found use in advanced technologies including electronic [1], electro-optical [2] and energy storage devices [3].

The electrical conductivity of composite films can be tailored to the specifications desired application over a wide range simply by changing the doping level / weight fraction of the conductive filler. Polyaniline is a promising candidate as a conductive filler for polymeric composite films, due to its environmental stability, reversible control of electrical properties and commercial availability.

Many researchers have reported supporting polyaniline composite with various insulating matrices, such as polyvinyl alcohol [4], polyvinyl chloride [5], polyacrylonitrile [6], nylon-6 [7] as well as the commercial ionomer, Nafion [8].

Recently, it has been reported that the hydrogen bonding between conducting polymers, e.g. polypyrrole, polyaniline etc. and host polymers such as polyvinyl alcohol, poly(bis-phenol carbonate) can be formed in conductive polymer composite systems [9,10]. This hydrogen bonding between conductive polymer and host polymer is

known to enhance the compatibility and physical properties of the composite.

Previously reported physical properties and doping characteristics of conductive polyaniline:nylon-6 composite, may be containing hydrogen bonding between PANI and nylon-6, because this bonding can be considered to affect the doping characteristics of the conductive polymer composite [7].

In this experiment, we have introduced a simple chemical route to fabricate electrically conductive films, using nylon-6,6 as supportive matrix and polyaniline (emeraldine base) as the electronically conductive polymeric filler. The resulting materials are environmentally stable and mechanically strong free-standing films.

4.2. Preparation of Conducting Polymer Composite Materials

The preparation of polyaniline:nylon-6,6 composite films were done by diffusing of aniline into nylon-6,6 matrix. Hence, a number of HCl doped polyaniline:nylon-6,6 composite film samples were prepared (**Table-3**). On the basis of higher electrical conductivity, mechanically strong film, PANI:Ny-6,6-5 was selected for further studies. For the determination of variation in electrical conductivity in PANI:Ny-6,6-5 due to the change in amount of nylon-6,6, four different samples were prepared as same temperature and time (**Table-4**).

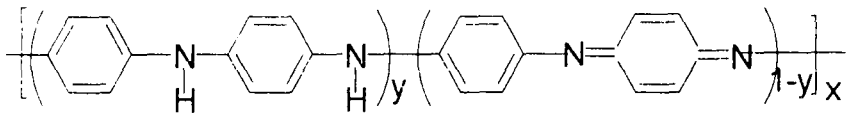
Table-3. Preparation details of HCl doped polyaniline:nylon-6,6 composites.

Sample ID	Temp (°C)	Time (h)	Weight of Nylon-6,6 (g)	Weight of film after soaking (g)	Amount of aniline soaked (g)	Amount of aniline soaked (%)	Weight of films after polymerization (g)	Color		σ (S/cm)
								As-prepared	HCl doped	
PANI:Ny-6,6-1	80	10	0.2658	0.2883	0.0225	8.4	0.2984	Light green	Light brown	Very low
PANI:Ny-6,6-2	80	15	0.2658	0.3108	0.0450	16.9	0.3217	Light green	Light brown	Very low
PANI:Ny-6,6-3	80	20	0.2658	0.3323	0.0675	25.3	0.3450	Green	Dark brown	$\sim 10^{-5}$
PANI:Ny-6,6-4	80	25	0.2658	0.3558	0.0910	33.8	0.3682	Green	Black	$\sim 10^{-3}$
PANI:Ny-6,6-5	80	30	0.2658	0.3783	0.1125	42.3	0,3916	Dark green	Black	$\sim 10^{-1}$

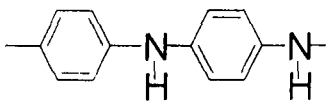
Table-4. Preparation details of HCl doped polianiline:nylon-6,6-5 composites at 80°C for 30 hour.

Sample ID	Temp (°C)	Time (h)	Weight of Ny-6,6 Film (g)	Amount of aniline soaked (%)	Weight of film after polymerization (g)	Thickness of the film after polymerization (mm)	σ (S/cm)
PANI:Ny-6,6-5a	80	30	0.1627	42.3	0.2396	0.40	0.121×10^{-1}
PANI:Ny-6,6-5b	80	30	0.1694	42.3	0.2416	0.43	0.262×10^{-1}
PANI:Ny-6,6-5c	80	30	0.1794	42.3	0.2643	0.45	0.134×10^{-1}
PANI:Ny-6,6-5d	80	30	0.2658	42.3	0.3916	0.47	0.275×10^{-1}

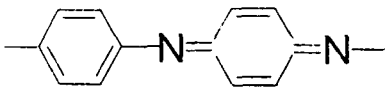
When the composite films were oxidized by potassium persulphate ($K_2S_2O_8$) in acidic media (HCl), the protonated conducting form of polyaniline (emeraldine salt) is produced as black color [11] shown in **Figure-29**.



It consists of reduced

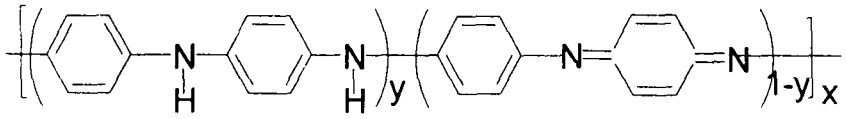


and oxidized



repeat units.

The "half oxidized" polymer (y = 0.5) is



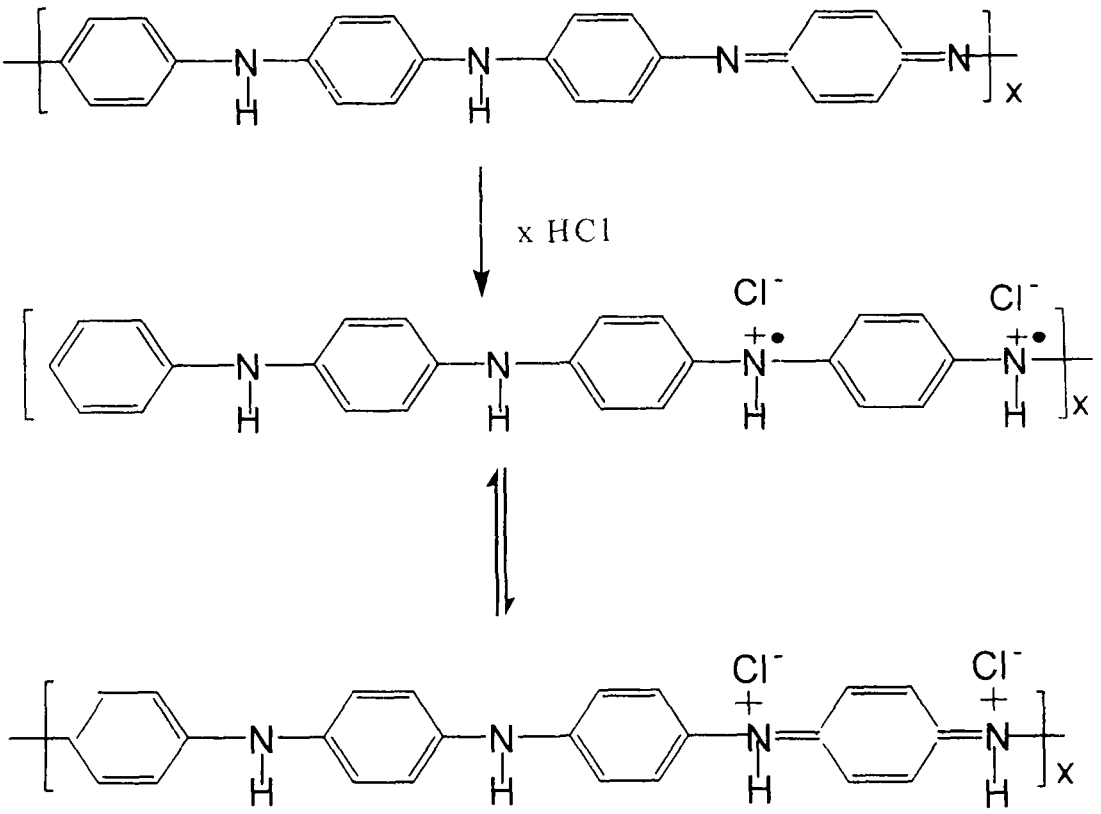


Figure-29. Chemical structure of emeraldinehydrochloride.

Schöllhörn and Zagefka [12] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides which has been further supported by the work of Foot and Shaker [13]. On the basis of disproportionation reaction of ammonia as suggested by F. Mohammad [14] for the undoping of polythiophene (PTH) by water. The overall chemical reactions are given in the following equation:

$$8NH_3 \longrightarrow 6NH_4^+ + 6e^- + N_2 \quad (28)$$

$$PTH^+\text{-}BF_4^- + NH_4^+ + e^- \longrightarrow PTH + NH_4BF_4 \quad (29)$$

$$6H_2O \longrightarrow 4H_3O^+ + 4e^- + O_2 \quad (30)$$

$$PTH^+\text{-}BF_4^- + H_3O^+ + e^- \longrightarrow PTH + HBF_4 + H_2O \quad (31)$$

$$HBF_4 \longrightarrow HF + BF_3 \quad (32)$$

The charge neutralization reaction depends on the rate of chemical reaction between the doped polymer and undoping agent. Which in turn will depend upon the reactivity of the polymer chain and basic strength of undoping agent [14]. The basic strength of water is very low, hence, it does not act as an effective undoping agent in the case of polyaniline, however, and an analogous neutralization reaction for the undoping of the polyaniline component of the composites by ammonia solution may be suggested as under **Figure-30.**

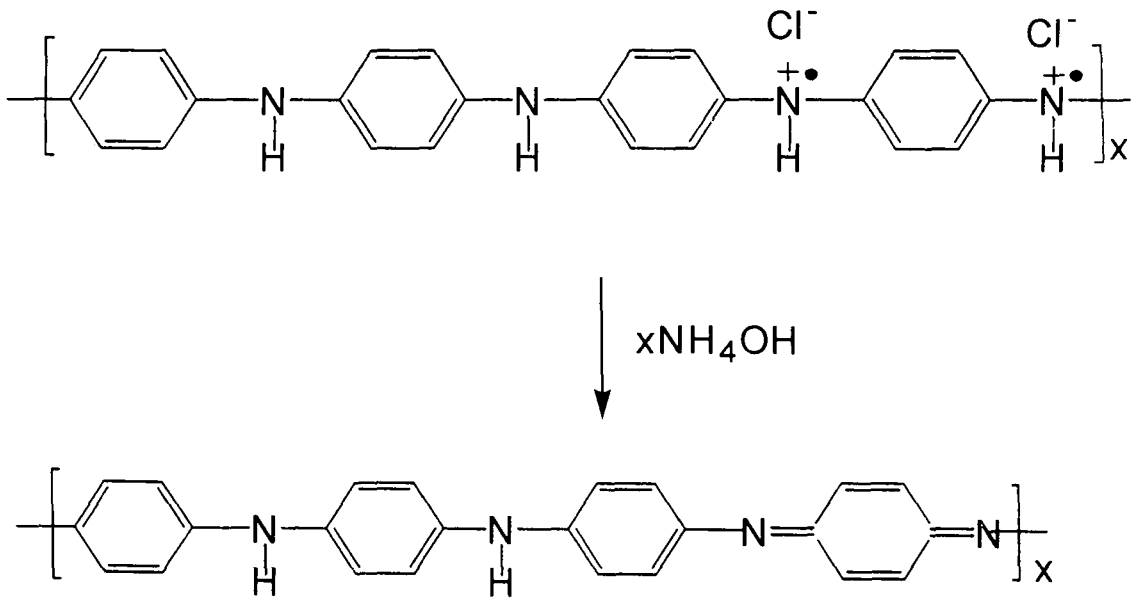


Figure-30. Undoping of emeraldine base.

$$NH_3 + H_2O \longrightarrow NH_4OH \qquad (33)$$

$$[(PANI\text{-}nH^+(Ny\text{-}6,6)][(nCl^-)] + nNH_4OH \longrightarrow$$
$$PANI(Ny\text{-}6,6) + nNH_4Cl + nH_2O \qquad (34)$$

Recently, it has been reported that PANI:Ny-6 composite film consisted layers, the outer layers were conducting composite layers and the inner layers was pristine nylon-6 [7]. In the similar way, it seems that polyaniline is mainly polymerized in the outer layer of the composite film (PANI:Ny-6,6) and that this layers retards the diffusion of the oxidant solution to the interior side and prohibits polyaniline from being polymerized inside the film or aniline does not diffuse deep inside the polymer matrix as absorved in the cross-sectional view of the films. Nylon-6,6 films got converted into gelly like mass if soaked above 80°C for longer periods of time.

4.3. Characterization

4.3.1. FTIR studies

The FTIR spectra of polyaniline:nylon-6,6 composites are presented in **Figure-31** and the tabulated from the FTIR peak positions are presented in **Table-5**. The band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene rings appears at 824 cm^{-1}. The bands corresponding to stretching vibration of N-B-N and N=Q=N structures appear at 1497 cm^{-1} and 1587 cm^{-1} respectively where –B- and =Q= stand for benzenoid and quinoid moieties in the polymer. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C-N bond appear at 1143 cm^{-1} and 1302 cm^{-1}.The band close to 1130 cm^{-1} is described as being characteristic of the conducting polymer due to the delocalization of electrical charges caused by deprotonation. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the polyaniline. The characteristic bands at around 688, 1642, 3303

cm^{-1} attributed to nylon-6,6 are present in all the composites. As-prepared polyaniline:nylon-6,6 composite showed a strong band around 1650 cm^{-1} corresponding to carbonyl group of nylon-6,6. For polyaniline, the band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene ring appears around 824 cm^{-1}. the bands corresponding to stretching vibration of N-B-N and N=Q=N structure appear around 1377 cm^{-1} and 1500 cm^{-1} respectively (where –B- ande =Q= stand for benznoid and quinoid moieties in the polymer). The band corresponding to stretching mode of C-N bond appears at 1504 cm^{-1} [15]. The gradual increase in the intensities of the bands corresponding to polyaniline and decrease in the intensities of bands corresponding to nylon-6,6 support the gradual change in the composition of the composite samples.

Table-5. FTIR peak positions (cm^{-1}) of PANI:Ny-6,6-3, PANI:Ny-6,6-4 and PANI;Ny-6,6-5.

PANI:Ny-6,6-3	PANI:Ny-6,6-4	PANI:Ny-6,6-5
3303	3302	3302
3077	3069	3078
2933	2930	2932
2858	2857	2858
2358	2356	2361
1637	1636	1637
1534	1538	1538
1473	1472	1473
1417	1416	1416
1368	1369	1367
1275	1273	1274
1198	1198	1198
1164	1164	1164
1145	1145	1144
937	933	934
934	829	825
826	687	687
688	578	578
579	530	530
531		

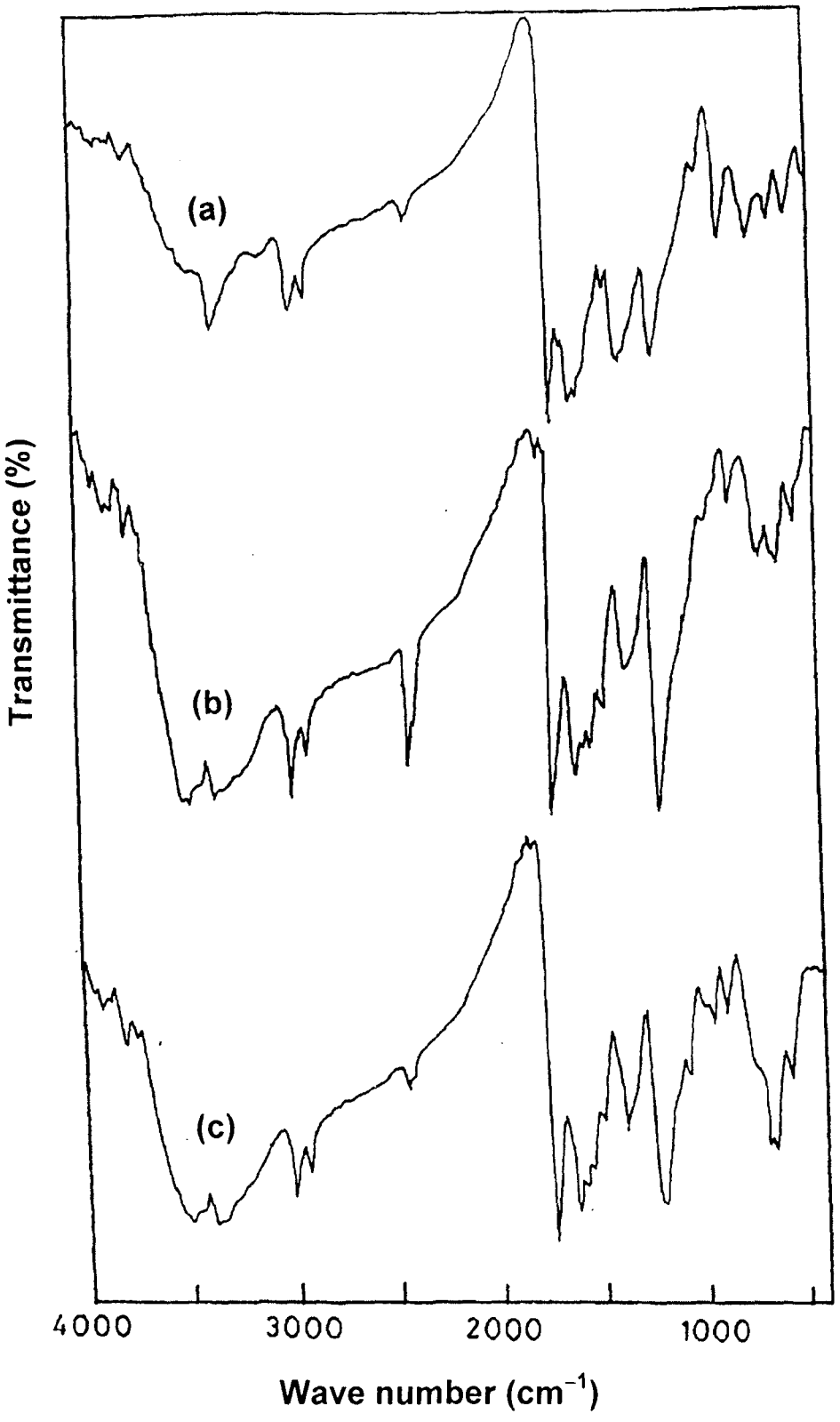


Figure-31. FTIR spectra of polyaniline:nylon-6,6 composites (a) PANI:Ny-6,6-3,(b) PANI:Ny-6,6-4 and (c) PANI:Ny-6,6-5.

4.3.2. SEM studies

Figure-32 shows the SEM photographs of polyaniline,nylon-6,6 and polyaniline:nylon-6,6-5 composites at different magnifications. Evidently, the homogeneous formation of composites of polyaniline in the nylon-6,6 matrix is observed.

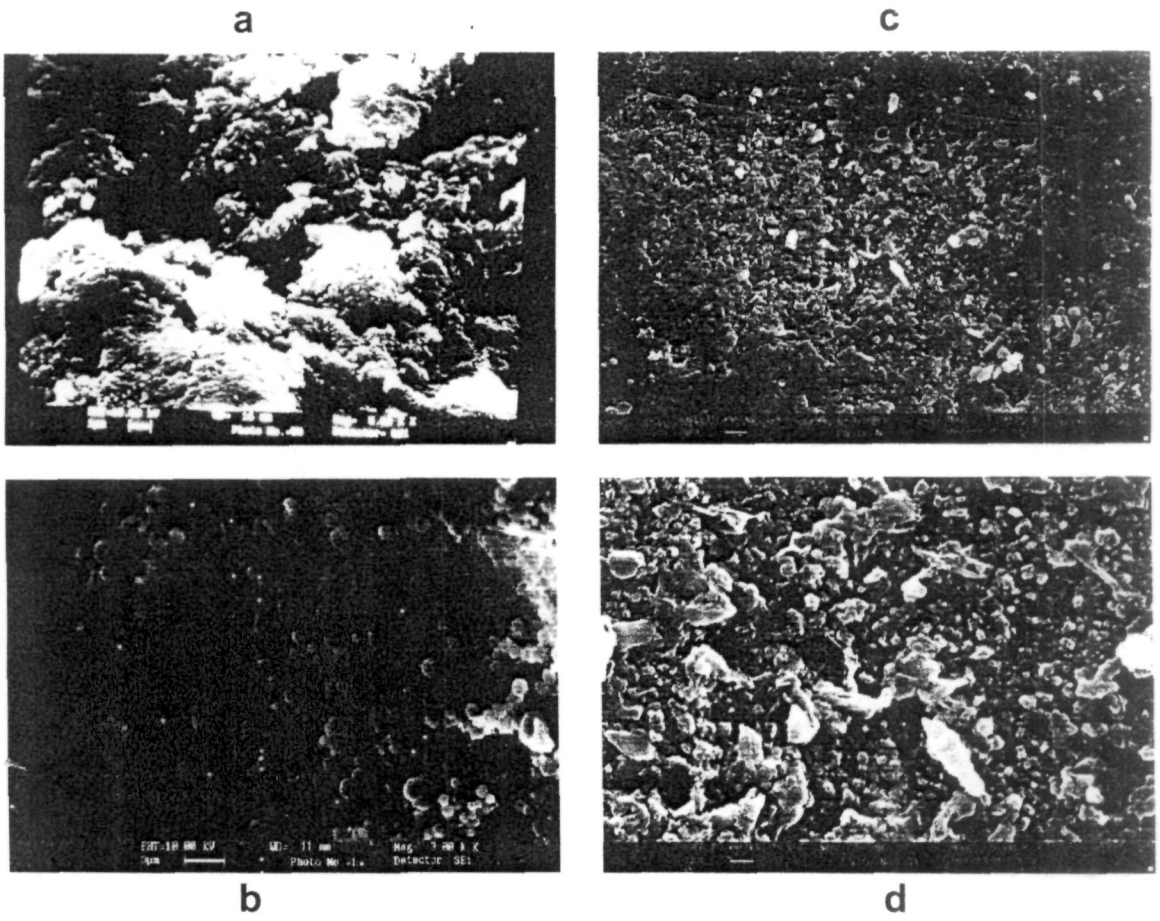


Figure-32. SEM photograph of (a) polyaniline, (b) nylon-6,6 (c) and (d) of PANI:Ny-6,6-5 composite film at different magnification.

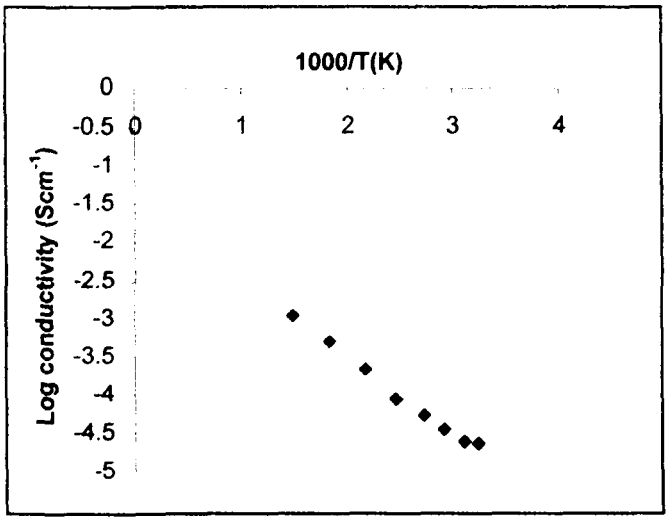
4.3.3. Electrical properties of composite films

The electrical conductivities of the composite films were measured from 30 to 100°C and were found in the semiconducting region, as presented in **Table-6.**

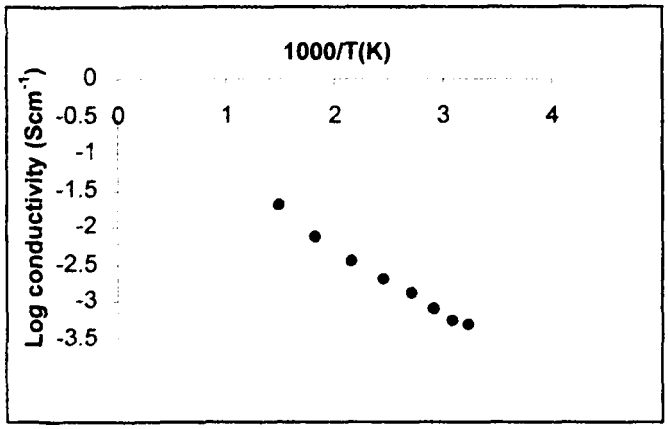
All the PANI:Ny-6,6 composite samples, in principle, followed the Arhenius equation for temperature dependence of electrical conductivity, as shown in **Figure-33.** This suggests the semiconducting nature of the HCl-doped composites. No semiconductor-to-metal transition was observed. However, the electrical conductivity of HCl-doped PANI:Ny-6,6-3 composite in the insulating region suggested that that the PANI concentration in this composite was well below the percolation threshold. The PANI:Ny-6,6-5 composite deviate from the Arhenius equation around 90°C and the electrical conductivity started decreasing after 100°C. This behavior was attributed to a semiconductor-to-metal transition and to the approach nearer to the glass-transition temperature of the composite.

Table-6. Temperature dependence of DC electrical conductivity (S/cm) of HCl doped polyaniline:nylon-6,6 composite films.

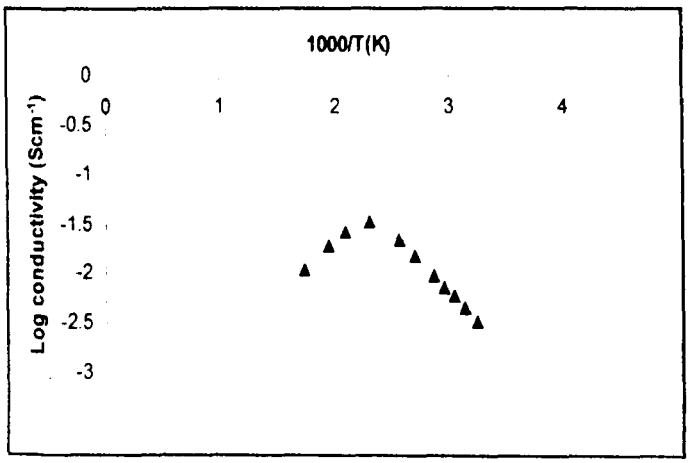
Sample ID → Temperature ↓		PANI:Ny-6,6-3		PANI:Ny-6,6-4		PANI:Ny-6,6-5	
(°C)	1000/T (K)	σ X10^{-5} (S/cm)	log σ	σ X10^{-3} (S/cm)	log σ	σ X10^{-1} (S/cm)	log σ
30	3.2467	3.1415	-4.64	0.4760	-3.322	00.8973	-2.468
40	3.1446	3.1945	-4.52	0.5645	-3.248	00.9285	-2.343
50	3.0487	3.2785	-4.45	0.6394	-3.100	01.1090	-2.140
60	2.9582	3.5012	-4.28	0.7553	-2.880	01.2730	-2.126
70	2.8735	3.8742	-4.05	0.8635	-2.690	01.9475	-2.010
80	2.9323	4.1581	-3.67	0.9497	-2.450	00.9858	-1.810
90	2.7173	4.2896	-3.30	1.1014	-2.140	01.0213	-1.660
100	2.6455	4.3761	-2.95	1.1954	-1.690	01.0487	-1.460
110	2.7732	-	-	-	-	01.0175	-1.580
120	2.5125	-	-	-	-	00.9642	-1.790
130	2.4213	-	-	-	-	00.8359	-1.960



(a)



(b)



(c)

Figure-33. Temperature dependence of log σ of (a) PANI:Ny-6,6-3 (b) PANI:Ny-6,6-4 and (c) PANI:Ny-6,6-5.

4.3.4. Thermal Stability in Terms of DC Electrical Conductivity Retention

Three samples, PANI:Ny-6,6-3, PANI:Ny-6,6-4 and PANI:Ny-6,6-5 were selected for the study of thermal Stability in terms of DC electrical conductivity retention. It was observed that the electrical conductivity of PANI:Ny-6,6 composites on exposure to HCl, due to doping of polyaniline component of the composite films, as evident from the following equation [16,17].

$$PANI(Ny\text{-}6,6) + n\,HCl \longrightarrow [(PANI\text{-}nH^{+}(Ny\text{-}6,6)][(nCl^{-})] \qquad (35)$$

The isothermal stability of the HCl doped films in term of DC electrical conductivity retention was carried out at 50°C, 70°C, 90°C, 110°C and 130°C in an air oven. The electrical conductivity measurements were done at an interval of 10 minutes in the accelerated ageing experiments. The electrical conductivity measured with respect to time of accelerated ageing is presented in **Figure-34**. The thermal stability was also studied by repeatedly measuring DC electrical conductivity with increasing temperature from 30 to130°C for five times at an interval of 40 minutes as shown in **Table-7**.

Table-7. Stability of polyaniline:nylon-6,6 composite films under isothermal conditions in terms of DC electrical conductivity retention.

Temp. (°C)	Time (min)	DC Electrical conductivity					
		PANI:Ny-6,6-3		PANI:Ny-6,6-4		PANI:Ny-6,6-5	
		σ X10^{-5} (S/cm)	$\sigma/\sigma°$	σ X10^{-3} (S/cm)	$\sigma/\sigma°$	σ X10^{-1} (S/cm)	$\sigma/\sigma°$
50	0	3.1415	1	0.4760	1	0.1673	1
	10	3.4183	1.0881	0.5883	1.2275	0.1984	1.1858
	20	3.6857	1.1732	0.6613	1.3892	0.2865	1.7124
	30	4.1264	1.3135	0.7352	1.5448	0.3674	2.1960
	40	4.3585	1.3813	0.7867	1.6527	0.4376	2.6156
70	0	4.4471	1	0.8356	1	0.5507	1
	10	4.5949	1.0331	0.8909	1.0661	0.5945	1.0795
	20	4.6847	1.0534	0.9183	1.0989	0.6498	1.1799
	30	4.8468	1.0898	0.9848	1.1785	0.7155	1.2992
	40	4.9932	1.1227	1.0612	1.2699	0.8234	1.4951
90	0	5.3486	1	1.1254	1	0.8576	1
	10	5.3976	1.0091	1.2586	1.1312	0.9013	1.0509
	20	5.4694	1.0225	1.3470	1.1969	0.9397	1.0957
	30	5.5804	1.0433	1.4794	1.3145	0.9534	1.1117
	40	5.6922	1.0466	1.5753	1.3997	0.9865	1.1503
110	0	5.6443	1	1.5634	1	0.9327	1
	10	5.3865	0.9543	1.4687	0.9394	0.8863	0.9502
	20	5.2436	0.9290	1.3896	0.8888	0.7628	0.8174
	30	5.1486	0.9121	1.2456	0.7967	0.6982	0.7485
	40	4.8475	0.8588	1.1508	0.7360	0.5196	0.5570
130	0	4.5753	1	0.9772	1	0.4275	1
	10	4.3545	0.9517	0.8286	0.8479	0.2974	0.6956
	20	4.1586	0.9089	0.7429	0.7602	0.1873	0.4381
	30	3.9467	0.8626	0.5843	0.5979	0.1186	0.2774
	40	3.7634	0.8225	0.3964	0.4056	0.0936	0.2189

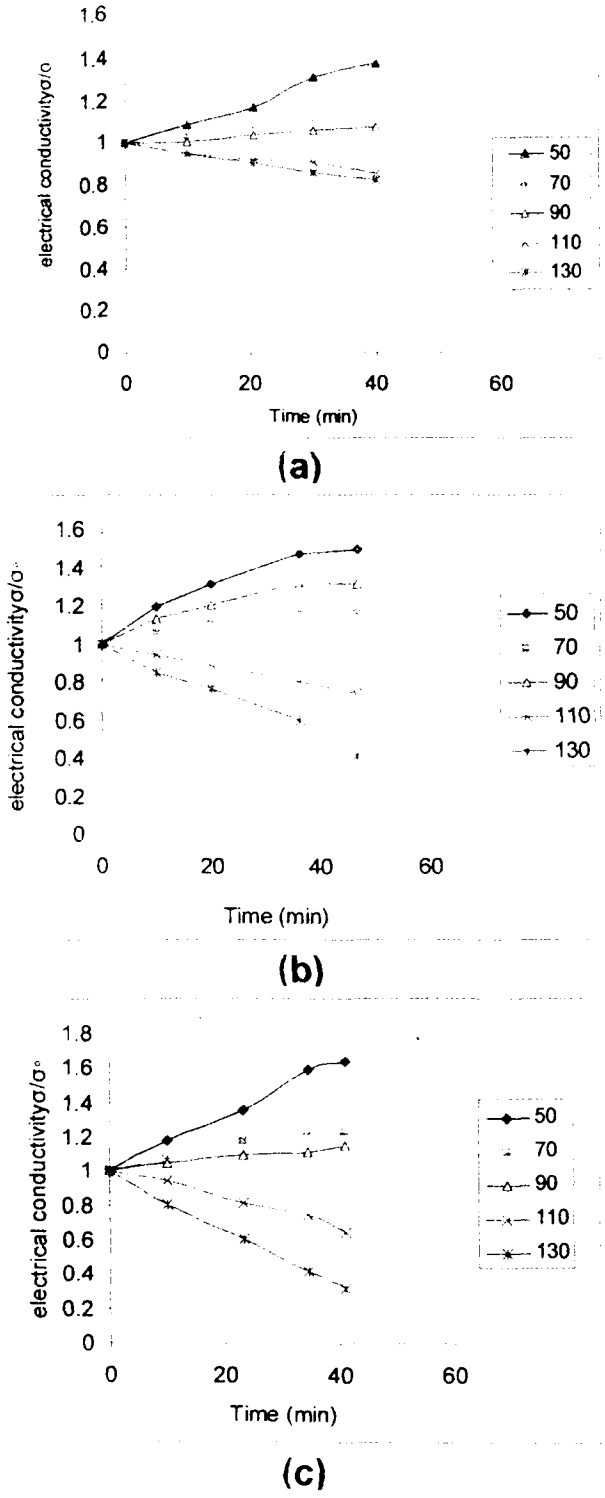


Figure-34. Stability in terms of DC electrical conductivity retention under isothermal conditions at 50, 70, 90, 110 and 130°C. (a) PANI:Nylon-6,6-3, (b) PANI:Nylon-6,6-4 and (c) PANI:Nylon-6,6-5.

The electrical conductivity of the polyaniline:nylon-6,6 films was measured from 30 to 130°C and found in the semi-conducting region. All the composite films followed Arhenius equation for the temperature dependence of the electrical conductivity from 30 to 115°C. After that a deviation in electrical conductivity was observed. A combination of all or some of the following factors could be responsible for the decrease in electrical conductivity beyond 130°C such as the loss of dopant, the chemical reaction of dopant with polyaniline or nylon-6,6 the semi-conductor to metal transition and the approaching of T_g. The studies on the stability of electrical conductivity under isothermal conditions at 50, 70, 90, 110 and 130°C showed that the electrical conductivity is more or less stable at 50, 70 and 90°C supporting the fact that all the composite films were sufficiently stable in term of DC electrical conductivity retention under ambient conditions below 90°C and the electrical conductivity decreases with respect to time at 110°C 130°C may be attributed to the loss of dopant and the chemical reaction of dopant with polymers. The stability in term DC electrical conductivity retention was observed to be fairly good as studied by isothermal technique. The polyaniline:nylon-6,6 composite films were found to be suitable for use in electrical and electronic applications below 90°C under ambient conditions.

4.4. Electrochemical Studies

4.4.1. Electrochemical cell no. 1.

It consisted of Zn anode and PANI:Ny-6,6 cathode of working area 2 cm^2 immersed in an aqueous solution of 1M $ZnCl_2$ at pH 5. It was used for the study of the variation of charging-discharging cycles.

When the cell was discharged by 140 mA current using 9-volt battery the voltage was first reduced sharply as shown in **Figure-35 (E-1)** which was followed by a gradual voltage drop until the oxidized PANI (emeraldine salt) form was completely changed to its reduced form and this discharging process completed in 45 minutes. The electrical conductivity by four-in-probe technique of the cathode film was found to be $2.3x10^{-2}$ Scm^{-1}. We assumed that the following reaction may be involved in discharging process of the cell under as (**Figure-36**).

When the cell was charged again by same current 140 mA, the voltage increased slowly as shown in **Figure-37(E-1)** and the reduced form of PANI (leucoemeraldine) changed to its oxidized form (pernigraline). There is a limit to the charging voltage. The charging process completed in 40 minutes and the electrical conductivity of the film was found to be $4.2x10^{-1}$ Scm^{-1}.

Since this reaction is reversible, the cell reaction during charging is the reverse of reaction during discharging.

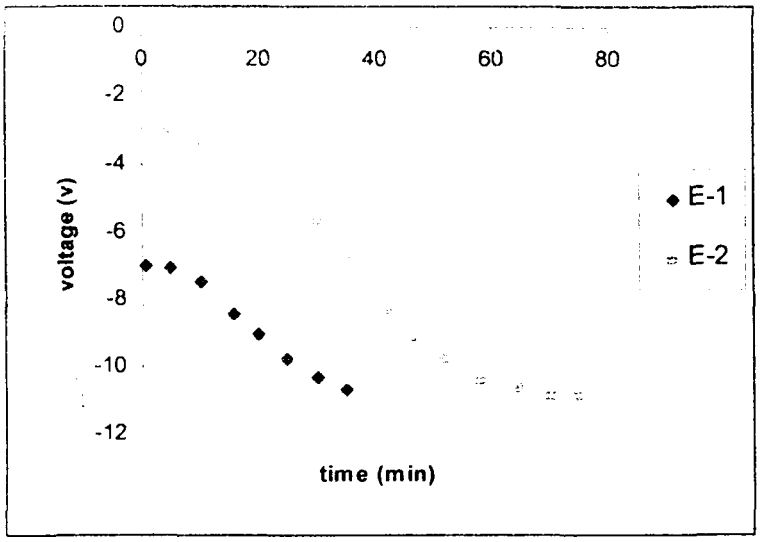


Figure-35. Voltage decreasing with time for discharging process in aqueous $ZnCl_2$ (E-1) and $AlCl_3$ in DMSO (E-2).

$$x\ Zn \longrightarrow x\ Zn^{2+} + 2x\ (e^-) \qquad (36)$$

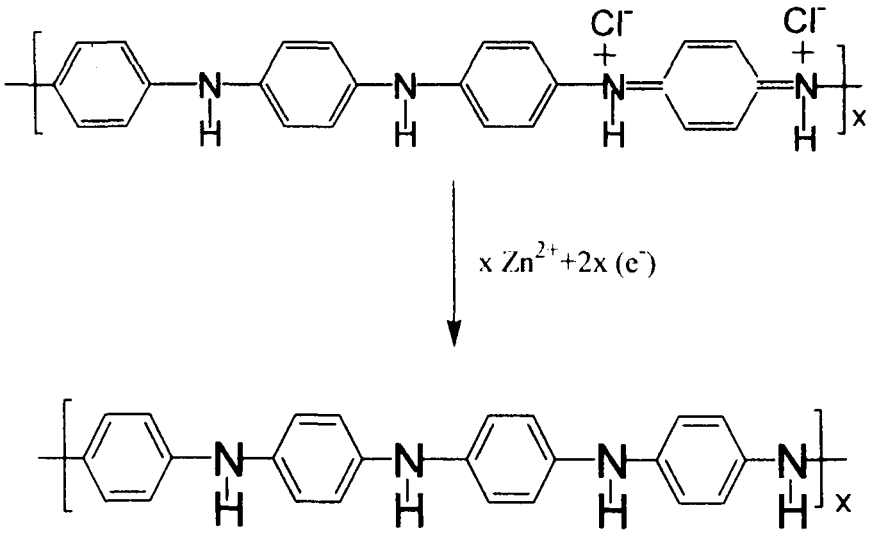


Figure-36. Reduced form of polyaniline.

Therefore, the over all discharging reaction of the cell is:

$$x\ Zn + 2\ PANI(Cl)_n \longrightarrow 2\ PANI + x\ Zn^{2+} + 2x\ Cl^- \qquad (37)$$

4.4.2 Electrochemical cell no. 2

It consisted of Al anode and PANI:Ny-6,6 cathode of working area 2 cm^2 immersed in non-aqueous solution of $AlCl_3$ (0.1M) in DMSO at pH 3.5. It was used for study of charging-discharging cycle. The cell discharged by using 140mA current. The voltage was reduced sharply as shown in **Figure-35 (E-2)** then voltage droped gradually and completly discharged in 75 minutes. The electrical conductivity of cathodic film was obesered to be $2.7x10^{-2}$ Scm^{-2}.

When the cell was charged to using 140mA, the voltage increased slowly as shown in **Figure-37 (E-2)** and charging process completed in 35 minutes and the conductivity of this film reached to$1.4x10^{-1}$ Scm^{-2}.

The cell voltage was simultaneously measured in galvanostatic conditions. PANI:Ny-6,6 composite films were investigated at 30°C as working electrodes for secondary cell containing either aqueous 1M $ZnCl_2$ or non-aqueous 0.1M $AlCl_3$ in DMSO electrolytes respectively showed almost similar behavior for PANI:Ny-6,6 composite films in acidic media.

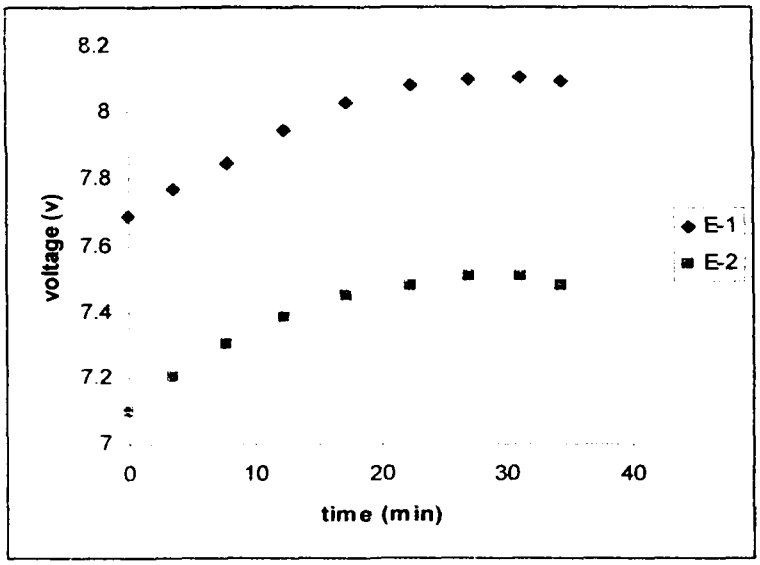


Figure-37. Voltage increasing with time for charging process in aqueous $ZnCl_2$ (E-1) and $AlCl_3$ in DMSO (E-2).

4.4.3. Electrochemical studies of diffusion into PANI:Ny-6,6 composite films

Diffusion of dopants into conducting composite film can also be measured electrochemically. The transport of ions into or out of a film can be followed by passing a short current pulse (5 seconds) to create an instantaneous excess, or deficit, of doping counter-ion on the surface of the film immersed in an electrolyte ($AlCl_3$ in DMSO) solution. By following the relaxation of the surface potential as the concentration of counter-ion returns to the equilibrium throughout the polymer, it is possible to determine the diffusion coefficient [18]. The diffusion coefficient was also measured as a function of doping level in the form of mol ratio of Cl^- per aniline rsidue. The diffusion coefficient decreases with increasing dopant ion concentration. The plot of potential versus time$^{-1/2}$ is linear and its slop yields the diffusion coefficient. The plots of the set of data **Table-8** from experiments on conducting composite films are given in **Figure-38**. Using this method, the diffusion coefficient of Cl^- into film was found to be 6.48×10^{-16} cm^2s^{-1}.

One concern, with measurements of this type, is that undoping of a film may result either from the outward diffusion of dopant counter-ions or from the inward diffusion of polymer co-ions, which would then form a salt within the film. This possibility has been avoided in our composite film study by measuring with doping pulse in sample which have only been doped in one direction, either reduction or oxidation.

The diffusion coefficient decreases with increasing dopant-ion concentration and increases with the size of dopant-ion. This suggests that some of the smaller anion may also be incorporated into the film, passively as dissolved salt and then removed during the undoping step.

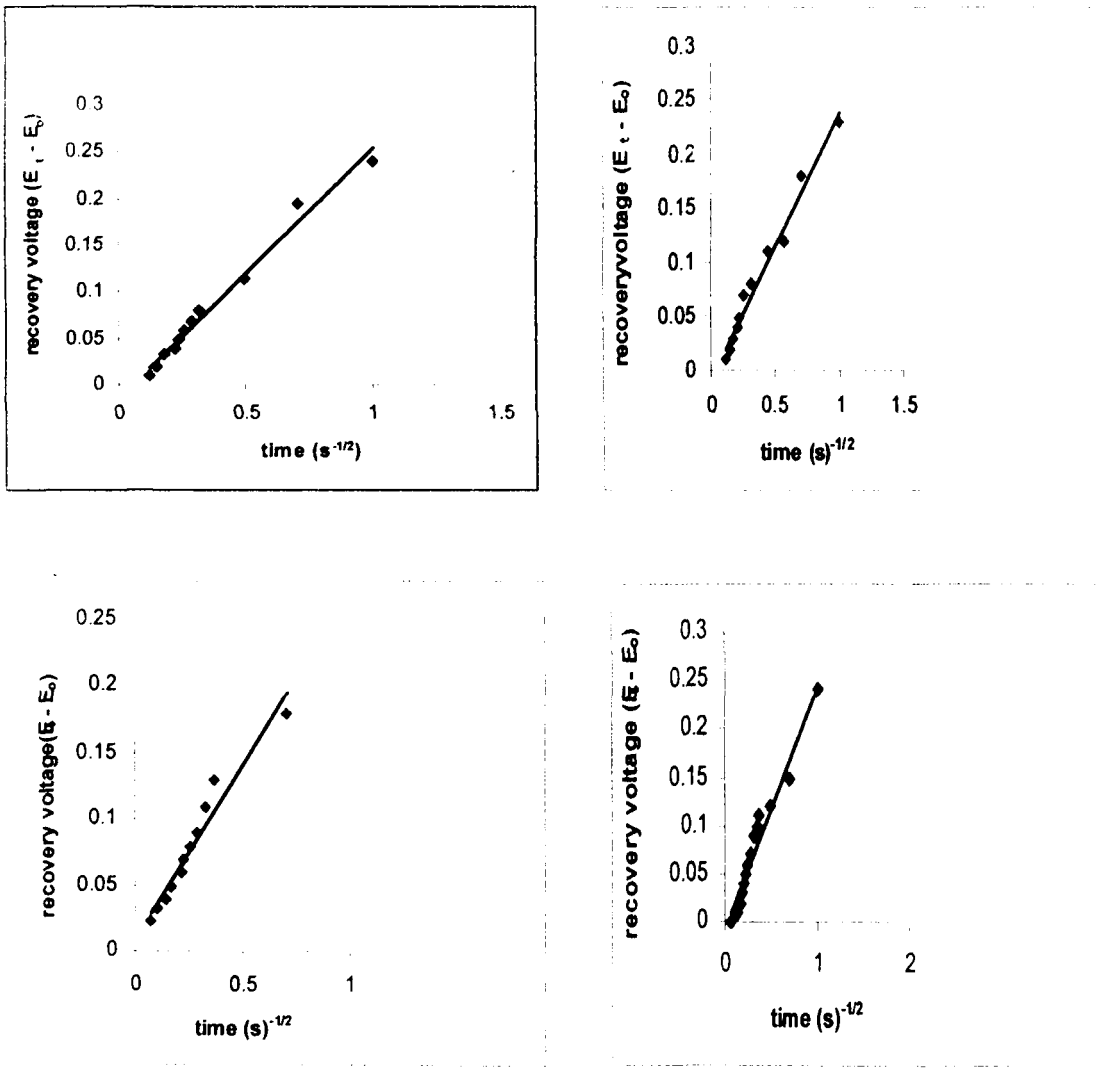


Figure-38. Diffusion behaviour of Cl^- intoPANI:Ny-6,6 composite films.

Table-8. Data obtained from diffusion behaviour of PANI:Ny-6,6 composite film.

E_o = 0.05 (20 DCV)		P = 5 (sec) Impulse	
t (sec)	E_t (Recovery Voltage)	$E_t - E_o$	$t^{-1/2}$
1	0.29	0.24	1
2	0.26	0.21	0.707
4	0.15	0.10	0.500
10	0.13	0.08	0.316
12	0.12	0.07	0.289
15	0.11	0.06	0.258
18	0.10	0.05	0.236
20	0.9	0.04	0.224
25	0.08	0.03	0.200
45	0.07	0.02	0.149
70	0.06	0.01	0.119

E_o = 0.04 (20 DCV)		P = 5 (sec) Impulse	
t (sec)	E_t (Recovery Voltage)	$E_t - E_o$	$t^{-1/2}$
1	0.27	0.23	1
2	0.22	0.18	0.707
3	0.6	0.12	0.577
5	0.15	0.11	0.447
10	0.12	0.08	0.316
15	0.11	0.07	0.258
20	0.9	0.05	0.224
22	0.08	0.04	0.213
30	0.07	0.03	0.182
40	0.06	0.02	0.158
70	0.01	0.01	0.119

E_o = 0.01 (20 DCV)		P = 5 (sec) Impulse	
t (sec)	E_t (Recovery Voltage)	$E_t - E_o$	$t^{-1/2}$
1	0.19	0.18	1
2	0.14	0.13	0.707
8	0.12	0.11	0.353
9	0.10	0.09	0.330
10	0.09	0.08	0.316
12	0.08	0.07	0.289
15	0.07	0.06	0.258
25	0.06	0.05	0.224
35	0.05	0.04	0.200
45	0.02	0.01	0.169
85	0.01	0.00	0.108

E_o = 0.01 (20 DCV)		P = 5 (sec) Impulse	
t (sec)	E_t (Recovery Voltage)	$E_t - E_o$	$t^{-1/2}$
1	0.23	0.22	1
2	0.14	0.13	0.707
4	0.11	0.10	0.500
7	0.10	0.09	0.378
8	0.09	0.08	0.353
10	0.08	0.07	0.316
12	0.06	0.05	0.289
17	0.05	0.04	0.242
20	0.04	0.03	0.224
22	0.03	0.02	0.213
25	0.02	0.01	0.200

Chapter-Five
Conclusion

CHAPTER-5

5. CONCLUSIONS

The results summarized in this work clearly establish the fact that the initial expectation of a large number of applications for conducting polyaniline composite has become a reality. Conducting polyaniline composites are now available as materials with a unique combination of properties: the important electronic and optical properties of semiconductors and metals combined with the attractive mechanical properties and processing advantages of the polymers. The field of conducting polyaniline composites has now attained a level of maturity consistent with a new set of opportunities to develop a wide range of applications based on conducting polyaniline as material for Industrial Products. With the outstanding progress made in their applications, there has been equally significant progress towards a deeper understanding of the basic condensed matter physics of the π-electrons in these conducting polymer materials. These two focal points have come together in the recent progress in the area of high quality polyaniline composites.

In the future, we can look forward to a deeper understanding of the physics of composite materials in the truly metallic regime and can also look forward to significant improvements in their properties. Since the current materials are strongly dominated by disorder. The field of conducting polyaniline composites is promising both from fundamental and technological points of view.

In this work, we have introduced a simple chemical route to fabricate conductive composite films. The composite films of polyaniline: nylon-6,6 were prepared by diffusion technique and the films used as cathode in self constructed electrochemical cells to estimate the diffusion coefficient of the dopant ions into the films.

The composite materials showed a remarkable increase in the electrical conductivity from insulator to conducting region after doping with hydrochloric acid. The isothermal stability in terms of DC electrical conductivity was also observed and the samples were found suitable for use in electrical and electronic applications below 100°C. The polyaniline:nylon-6,6 composite films so formed were successfully used as an electroactive cathode material in electrochemical cells. Although, chemical doping via acid base chemistry was more efficient, method a successful attempt was made to undope and dope electrochemically the chemically synthesized polyaniline:nylon-6,6 composite films.

The electrochemical cell model thus constructed was a wet type battery in which the electrolyte was aqueous $ZnCl_2$ or non aqueous $AlCl_3$ in organic solvent (DMSO). The fact that the electrochemical processes of the secondary batteries involve the interconversion of a chemical energy into electrical energy and vice versa. During the discharging of the cell, the anion (Cl^-) is released from the cathode and the cation (Zn^{2+}/Al^{3+}) is dissolved from the anode and vice versa in case of charging. Therefore, during discharging and charging, diffusion of both metal ions as well as the anion takes place into and out of the film. The extent of the dopant ion present in the polyaniline composite films was essentially calculated and the diffusion coefficient of the

diffusing ion was estimated employing the galvanostatic pulse technique. Diffusion of Cl^- into the polyaniline:nylon-6,6 composite films was of Fickian type, yet the estimation study could further be improved.

5.1. Future Suggestions

The work so far has been with poorly characterized materials hence, there is a need for better characterization to understand various phenomena taking place in composite films and to estimate work in the following directions.

1. The polyaniline is mainly polymerized in outer layer of the host matrix, aniline does not diffuse deep inside the polymer matrix.

2. The study of the cause of decrease in conductivity of stored samples of polyaniline composites with time, which may be attributed due to the loss of dopant, the chemical reaction of dopant with polymer or oxidative degradation of composites.

3. To improve battery reversibility and stability in aqueous solution, increase coulombic efficiency and self-discharge rate of the cell and the life cycle of PANI secondary batteries by means of electrochemically and surface analysis techniques.

4. The effect of different factors on the diffusion coefficients of ions into composite films, such as temperature, diffusant size and concentration, diffusant solubility in the polymer, electrostatic interactions and impurities etc.

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